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Degradation of graphene coated copper in simulated proton exchange membrane fuel cell environment: Electrochemical impedance spectroscopy study

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HIGHLIGHTS

- Graphene coatings are deposited on copper bipolar plates of PEMFC by CVD.
- The degradation of graphene coated copper in sulfuric acid is investigated by EIS.
- The charge transfer resistance of graphene coating is ~3 times greater than copper.
- The excellent conductivity of graphene enhances its corrosion resistance.

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ABSTRACT

Metallic materials are most suitable for bipolar plates of proton exchange membrane fuel cell (PEMFC) because they possess the required mechanical strength, durability, gas impermeability, acceptable cost and are suitable for mass production. However, metallic bipolar plates are prone to corrosion or they can passivate under PEMFC environment and interrupt the fuel cell operation. Therefore, it is highly attractive to develop corrosion resistance coating that is also highly conductive. Graphene fits these criteria. Graphene coating is developed on copper by chemical vapor deposition (CVD) with an aim to improving corrosion resistance of copper under PEMFC condition. The Raman Spectroscopy shows the graphene coating to be multilayered. The electrochemical degradation of graphene coated copper is investigated by electrochemical impedance spectroscopy (EIS) in 0.5 M H_2SO_4 solution at room temperature. After exposure to the electrolyte for up to 720 h, the charge transfer resistance (R_t) of the graphene coated copper is ~3 times greater than that of the bare copper, indicating graphene coatings could improve the corrosion resistance of copper bipolar plates.

1. Introduction

The proton-exchange membrane fuel cell (PEMFC) is a promising power generation system which converts the chemical energy of hydrogen and oxygen (or air) into electricity with water as the only byproduct. However, the high cost of materials, such as bipolar plates and catalyst used in PEMFC limit its commercial application. The bipolar plates made of graphite and graphite composites are heavy and expensive to manufacture, and which respectively account for ~80% of the total weight and ~45% of the stack cost [1]. Metallic bipolar plates possess excellent electrical conductivity, high strength, low gas permeability and can be manufactured in light weight at low cost. Consequently, the volume and weight of a PEMFC can be decreased along with the increase in the power density of the fuel cell stack. Stainless steel [2,3], titanium [4,5], aluminum [6,7], copper [8–10] alloys are among the metallic materials that have been investigated for bipolar plate materials for PEMFC. However, the degradation of metallic bipolar plates under the weakly acidic environment of a PEMFC (pH 2–4) has emerged as a serious problem [11]. A variety of coatings with high corrosion resistance and electrical conductivity have been developed to protect the metallic bipolar plates that include both carbon-based

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and metal-based coatings [12]. The investigated metal-based coatings include noble metals and metal nitrides/carbides [13–15]. Carbon-based coatings include graphite, conductive polymer and diamond-like carbon [16–18]. The conductive polypyrrole/polyaniline bilayer coatings were also investigated for 304 stainless steel bipolar plates of PEMFC [16]. However, the bilayer suffered reduction at the anodic potential of PEMFC, which decreased the conductivity of the polymer. Therefore, the stability of conductive polymer coatings in the environment of PEMFC needs further improvement. Carbon or graphite possesses the excellent chemical stability and conductivity. However, it is difficult to deposit electrically conductive carbon or graphite thin film, since the carbonaceous thin-film is often too loose to serve as a barrier layer for corrosive solution [19].

Graphene is an atomically thin film of a honeycomb network of sp^2 hybridized carbon atoms, which has been deposited successfully on Ni or Cu by chemical vapor deposition (CVD) [20,21]. Different studies have showed that graphene coatings could improve the corrosion resistance of metals such as Ni or Cu in aqueous solution [22–24]. Besides its excellent corrosion resistance, graphene also possesses excellent conductivity and hydrophobicity [25]. Therefore, researchers have investigated use of graphene for the protection of metallic bipolar plates of PEMFC [26,27]. In PEMFC, the sulfate anions (SO_4^{2-}) that are produced upon the membrane degradation release into fuel cell system and attack the metallic bipolar plates [28]. However, fewer reports focus on the corrosion of the graphene coated metallic substrates in the acid solution containing sulfate anions [29].

In this paper, the corrosion resistance of graphene coated Cu in H_2SO_4 solution has been investigated for the purpose of potential application of graphene as conductive coating that can also provide protection to metallic bipolar plates of a PEMFC against corrosion.

2. Experimental procedures

2.1. Deposition of graphene coatings

Coupons (13 mm × 13 mm x 0.1 mm) of Cu (99.96%, The Nilaco Corporation no. 113321) were polished and cleaned using acetone, followed by the dry air blowing to clean up the solvent residue and dirt. Subsequently, CVD growth of graphene on the Cu substrate was performed by the reported procedure [30]. However, further optimized conditions are shown as in the PhD work of one of the co-authors (M.R.Anisur) [31].

2.2. Electrochemical impedance spectroscopy(EIS)

EIS measurements were conducted in a three-electrode cell with a saturated calomel electrode (SCE) as the reference electrode, Pt mash as counter electrode, and uncoated or graphene-coated copper as working electrode. All electrochemical experiments were carried out in 0.5 M H_2SO_4 solutions at room temperature. Open circuit potential (OCP) was monitored for at least 1 h to confirm its stability with time and a fluctuation of OCP within 10 mV for a period of 1000 s was considered as a stable potential before carrying out the electrochemical measurements. The impedance was measured at frequencies between 1 MHz and 10 mHz, recording 10 points per decade of frequency using the Biologic potentiostat and EC Lab software. For reproducibility, two samples were used in the two distinct reproduced measurements.

2.3. Surface morphology and coating characterization

2.3.1. Raman spectroscopy

Raman spectra of graphene coated Cu was obtained using Renishaw Invia Raman spectrometer equipped with 514 nm wavelength green laser (10% of laser power) and 1 μm spot size under a 50× objective.

2.3.2. Scanning electron microscopy (SEM)

The morphology of the graphene coated Cu and the bare Cu before and after electrochemical test in 0.5 M H_2SO_4 was observed using JEOL JSM-7001F FEGSEM with an accelerating voltage of 15 kV.

3. Results and discussion

3.1. Raman spectroscopy of graphene coated copper

The Raman spectroscopy of graphene coating is shown in Fig. 1. Graphene layers typically display sharp G (1580 cm^{-1}) and 2D (2650-2700 cm^{-1}) bands [32,33], and the first-order D peak reflects the defects in the graphene [34]. A weak D-peak located at 1370 cm^{-1} could be observed that correspond to the defects and structural imperfections in the graphene lattice. For a single layer graphene, the G/2D intensity ratio should be ~0.36 while the multilayered graphene has a higher G/2D ratio as well as 2D band shape is somewhat altered [35]. The ratio of I_G/I_{2D} of as-deposited graphene is about 1.09, indicating that a multilayered graphene was deposited [28].

3.2. Surface morphology of graphene coated copper

Fig. 2 shows the morphology of the bare and graphene coated copper. The bare copper surface is relatively flat and undisrupted. The graphene coating on the copper has some obvious ripples and folds. Fasolino [36] suggested that such ripples that spontaneously develop in the graphene coatings have heights in the range of 50–100 Å, which is attributed to thermal vibrations and interactions between carbon atoms that render them to occupy in the third dimension. The folds in the as-deposited graphene suggest the inhomogeneous nature of the coating whose thicknesses varies across the surface, as also reported in other study [37]. An immersion of uncoated copper in corrosive electrolyte for 192 h causes severe corrosion and undercutting along grain boundaries, to the extent of grains falling out, as seen in Fig. 2c. In contrast, the graphene coated copper appears largely unattacked even after a much longer immersion for 720 h in 0.5 M H_2SO_4 solution. No blisterings or delaminations are observed in the graphene coating on the copper.

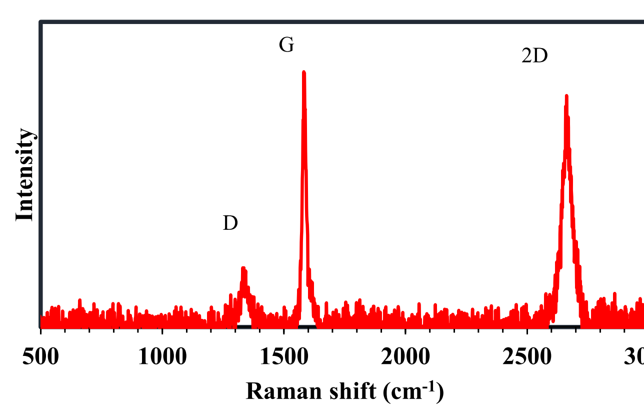

Fig. 1. Raman spectroscopy of graphene coated copper.