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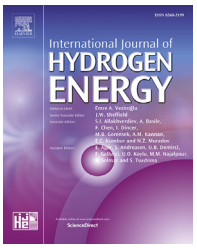

The corrosion behavior and mechanical properties of CrN/Ni–P multilayer coated mild steel as bipolar plates for proton exchange membrane fuel cells

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ABSTRACT

This research mainly studies on the interfacial conductivity and corrosion resistance of mild steel (MS)/electroless plating nickel (EN)/CrN composite coating. The MS/EN/CrN composite coating is deposited on a mild steel substrate using a combination of electroless nickel plating process and closed field unbalanced magnetron sputter ion plating system. The simulative working environment of proton exchange membrane fuel cell (PEMFC) is implemented to test the electrical and corrosion properties of uncoated mild steel and coated samples. Results show that the performance of the MS/EN/CrN coated samples was greatly improved. The SEM results indicate that the surface of MS/EN/CrN is dense and smooth. CrN (111) and Ni (111) are observed in the MS/EN/CrN coating by XRD. The potentiodynamic polarization and EIS tests show that the incorporation of electroless nickel deposits into the CrN coating can provide better corrosion resistance. Potentiostatic polarization tests reveal that MS/EN/CrN coating has the lowest current density both in anodic and cathodic environment. The Interfacial contact resistance (ICR) results show that the ICR of MS/EN/CrN coated sample reduces to 3.3 mΩ cm^2 at a compaction force of 140 N/cm^2. Moreover, after potentiostatic polarization, the ICR values of the MS/EN/CrN coating are still less than DOE's 2020 target. In addition, compared with other samples, the hardness and adhesion property of the MS/EN/CrN multilayer coating were greatly improved, which is beneficial for resisting the shock and wear during the assembly process of fuel cell stacks.

Introduction

The bipolar plates (BPs), one of important component for a typical proton exchange membrane fuel cell (PEMFC), can provide the electrical connection from cell to cell, distribute reactant gases homogeneously though flow field, conduct the electrical current away from each cell, promote the residual water remove from the outlet of the cell, and facilitate thermal management [1–4]. Furthermore, previous reports have demonstrated that BPs account for about 80%–85% of the total weight and about 30% of the total cost of the PEMFC stack respectively [5,6]. Therefore, it is necessary to investigate the reduction of weight and cost of bipolar plate materials to lessen the total cost and mass of PEMFC stack. Technically, the bipolar plates must possess properties such as high chemical stability, good electrical conductivity, and good corrosion resistance,

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high thermal conductive, low contact resistance to the backing, good mechanical strength, and low gas permeability [7–9]. However, few materials can satisfy all the desired nature of bipolar plate. Currently, graphite and its composites have been widely used to fabricate these bipolar plates because of their good corrosion resistance, high electrical conductivity, and low surface contact resistance [7,10]. Unfortunately, they are brittle and lack mechanism strength, and have high gas permeability as well as relatively high cost for machining gas channels, which is the main limitation to their widespread commercial applications [11–13]. Hence, metals have been considered as an attractive substitute for traditional graphite-based materials because of their good electrical conductivity, low gas permeability, low cost, easy manufacturing, and suitable mechanical properties [14–16]. Up to now, the most intensively studied metallic materials for bipolar plate is stainless steel because of its good mechanical strength and good corrosion resistance [17,18]. As compared to stainless steel, mild steel has advantages of low bulk electrical resistivity (a fifth of stainless steel), high heat conductivity (2.8 times higher than stainless steel at 100 °C), and low manufacturing cost. Nevertheless, corrosion resistance of common mild steel in PEMFC electrolyte (pH 3–4) is poor, and metallic positive ions generated by corrosion of mild steel can permeate to the proton exchange membrane and degrade its performance [19,20].

In previous reports, to improve the corrosion resistance of mild steel, various coatings with high corrosion resistance and conductivity were applied to withstand the aggressive PEMFC environments. M.H. Mathabatha et al. [21] deposited zinc-based alloy coatings on mild steel substrate by plasma spraying technique and indicated that the zinc-based alloy coated mild steel got an obvious improvement in the corrosion resistance and micro hardness properties as compared to the uncoated mild steel substrate. V. Vitry et al. [22] deposited Ni–P and Ni–B coatings by electroless deposition and indicated that Ni–P or Ni–B coated mild steel substrate exhibited better corrosion resistance and mechanical property in comparison with bare mild steel. The difference in corrosion resistance between Ni–P (Ni–B) coated substrates and uncoated mild steel can be explained by the formation of hypophosphite due to the oxidation of the phosphorus present at the coating surface. This study showed that electroless deposition is a good method which could produce homogeneous coating with good adhesion and corrosion resistance on various substrate materials. Fetohi A E et al. [23] evaluated the corrosion resistance of electroless Ni–P coating on pure Al, Al 6061, Al 3004 and Al 1050 in an environment simulated to PEM fuel cell, and they found the lowest corrosion current density values were observed for coated Al 1050 substrate. However, the values of interfacial contact resistance and potentiostatic polarization remained high for all coated samples, which showed single electroless Ni–P coating didn't provide adequate protection against electrochemical corrosion in a simulated fuel cell environment. Sung-Ying Tsai et al. [24] produced a hydrophobic Au-PTFE/Ni–P multilayer coating on Al-alloy 5052 substrate for an application in bipolar plates using the electroless nickel immersion gold technique, and the polarization results showed that Au-PTFE/Ni–P multilayer coatings exhibited a lower corrosion current density and a more positive corrosion potential than monolayer Ni–P coating. However, Au coated samples is much more expensive compared to Ni–P coated samples. Previous research has shown that metal nitrides are potential materials for surface modification such as CrN, TiN, and CrTiN owing to their good corrosion resistance, excellent interfacial conductivity and low cost [25–27]. According to the study of Min Zhang et al. [28], the performances of CrN hard coatings with the charge of nitrogen content in coating and the contact resistance values reached the minimum while the content of nitrogen in the coating was 35.3%. S.H. Lee et al. [29] investigated the electrical conductivity and corrosion properties of CrN- and TiN-coated SS316L and found that they exhibited lower ICR value. Yan Mao et al. [30] fabricated a C/Cr film with electroless nickel interlayer (C/Cr/Ni) on the magnesium alloy and found that the corrosion potential (E_{corr}) of the C/Cr/Ni coated magnesium alloy was about −1.37 V vs saturated calomel electrode (SCE) in contrast to about −1.67 V vs SCE of the bare one in 3.5 wt % NaCl solution. The corrosion current density of C/Cr/Ni coated magnesium alloy was reduced from 186 $mAcm^{-2}$ to 11 $mAcm^{-2}$ (uncoated magnesium alloy substrate). Jiann-Shiung Chen et al. [31] found the combination of an electroless Ni–P interlayer with PVD CrN coating on a mild steel substrate exhibited promising results in adhesion and corrosion tests. It is reported that the CrN/Ni–P/MS multilayer coating exhibits a better corrosion resistance compared to bare mild steel substrate in 0.5 M NaCl solution. The electroless Ni–P interlayer was selected as the enhancement layer in these composite coatings considering the good corrosion resistance and electrical conductivity of Ni–P layer. However, no literature is available on the research of the corrosion behavior of CrN or CrN/Ni–P coated mild steel substrate in PEMFC working environment until now. In this study, the corrosion behavior and electrical conductivity of CrN/Ni–P coatings were investigated in simulated PEMFC environment. The final goal is to improve the corrosion resistance of mild steel substrate and obtain basic information for the development of CrN/Ni–P coated mild steel substrates as BP material candidates.

Experimental

Material preparation

Commercially available mild steel with a size of $20 \times 20 \times 3$ mm^3 were used as the substrate materials to be deposited. The mild steel chemical composition (in wt%) is 0.21 C, 0.43 Mn, 0.28 Si, 0.031 S, 0.022 P, and the balance Fe. The samples were mechanically ground by the SiC papers (#400 grits, #800 grits, #1200 grits and #2000 grits, respectively) and mechanically polished with diamond abrasion paste. The samples were ultrasonically cleaned in acetone and ethanol for 20 min separately, followed by drying in warm Air. Prior to the electroless nickel deposition, the substrates were alkaline degreased in a NaOH base solution (40 g/L NaOH, 25 g/L Na_2CO_3, 7 g/L Na_3PO_4, and 3 g/L Na_2SiO_3) for 25 min at 85 °C, and cleaned with deionized water. Then the cleaned substrates were activated in acid solution with 10 vol % H_2SO_4 for 30 s at room temperature to remove oxide film from the surface of samples, and the mild steel substrates were cleaned with deionized water again. After rinsed in distilled water, the sample was dipped into the electroless Ni plating solution to

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