INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–13

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Effects of Mo content on the interfacial contact resistance and corrosion properties of CrN coatings on SS316L as bipolar plates in simulated PEMFCs environment

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ARTICLE INFO

Article history:
Received 31 January 2018
Received in revised form
7 April 2018
Accepted 8 April 2018
Available online xxx

Keywords:
Proton exchange membrane full cells (PEMFCs)
CrMoN films
Surface morphology
Corrosion resistance
Electrochemical impedance spectroscopy
Corrosion mechanism

ABSTRACT

CrMoN films with different Mo contents are deposited on SS316L by closed filed unbalanced magnetron sputtering ion plating (CFUBMSIP) to investigate corrosion resistance and electrical conductivity. The sputtering current of Mo target was altered to obtain various Mo contents. The result of SEM confirms that CrMoN coatings have a dense and uniform microstructure. X-ray diffraction (XRD) result shows that CrMoN coated samples have a preferred orientation of (111) direction. Interfacial contact resistance (ICR) between bipolar plate and gas diffusion layer (GDL) decreases with Mo incorporation, and CrMoN-4A coated sample has the lowest ICR value of 5.8 mΩ cm^2 at 1.4 MPa. The result of potentiodynamic polarization test in the simulated PEMFCs environment shows that incorporation of Mo doped CrN coating can obviously improve the corrosion resistance of samples and CrMoN-4A has the highest corrosion potential which is 0.1341 V in simulated PEMFCs cathode environment. Electrochemical impedance spectroscopy (EIS) result indicates that the incorporation of Mo can improve better corrosion resistance, and CrMoN-4A has the highest corrosion resistance. The corrosion mechanism of coating also has been investigated.

Introduction

PEMFCs has been considered as a perfect device for it can directly convert chemical energy to electrical energy with zero emission, low operating temperature and high power density [1,2]. Bipolar plate is one of the most important part in PEMFCs stack which can distribute reactants, separate oxidant and reductant, collect current from each cell, remove residual water and facilitate thermal management [3]. Besides, bipolar plate takes up the 30% of total cost and 80% weight of PEMFCs, respectively [4–6]. The bipolar plate must possesses excellent electrical conductivity, good mechanical strength, high corrosion resistance and good gas impermeability [7]. Graphite and graphite composites were used as bipolar plate because of their good chemical stability and current conductivity in PEMFCs environment in early time. However, graphite's poor manufacturability, permeability and brittleness limits its commercial application [8–10]. To replace graphite bipolar plate, various materials have been studied. Stainless

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https://doi.org/10.1016/j.ijhydene.2018.04.044

steel is considered as bipolar plate on account of their good electrical conductivity, low cost and high mechanical stability [11]. It's also easy to fabricate flow channels on stainless steel [12]. Nevertheless, stainless steel tend to be dissolved and corroded when exposed to an operating harsh acid (pH 3-4) PEMFCs environment at the operation temperature [13]. Besides, passive film formed on the surface of SS316L will lead to the increase of interfacial contact resistance. Meanwhile, the metal ion dissolved in the solution would pollute the catalyst and membrane electrode assembly (MEA) [14,15].

In previous studies, Surface modification technology such as chemical vapor deposition (CVD) [16], physical vapor deposition (PVD) [17], ion implantation [18], spraying [19], and surface nitridation [20] have been used to depositing coating on the substrate. Such as metallic coating [21,22], metal nitrides [23,24], polymer coatings [25,26], carbon based coating [27,28] are investigated, respectively. Gao et al. [29] deposited nickel-phosphorous coatings on titanium substrate with the help of electrochemical promotion. The result showed that the Ni–P coating prepared with a current density of 1.1 A dm^{-2} at 55 °C has the best corrosion resistance. Zhang et al. [30] used PVD coating technique to deposite Cr/CrN multiple coating on SS316L. The ICR of CrN coating under 1.4 MPa was 8.4 mΩ cm^{-2}. Cr/CrN multilayer had a corrosion current density which was 10^{-8} A cm^{-2} at 0.6 V (0.5 M H_2SO_4 + 5 ppm HF solution at 70 °C with air). Lee et al. [31] deposited TiN and CrN coating on SS316L by cathode arc ion plating. The result showed that the corrosion current density of CrN was 0.1 μA cm^{-2} at 0.6 V (cathode environment). However TiN film was easily damaged in acid solution. The ICR of TiN (10 mΩ cm^{-2}) and CrN (23 mΩ cm^{-2}) at 150 N cm^{-2} were lower than bare SS316L.

The single layer can obviously improve the anti-corrosion property of bare SS316L. However, the coatings deposited by PVD technology have inherent defects which will degenerate the performance of coatings [32]. It has been confirmed that the ternary coatings show better corrosion resistance than single layer as the added element can reduce the number of pinholes and particles. So Ternary coatings and element incorporation can effectively prevent corrosion and improve electrical conductivity [33]. Researchers have added various elements such as Al, Si, C, Ti, Zr [3,34–37] into CrN crystal structure to investigate the property of Cr-X-N multilayer coatings. Yi P et al. [35] deposited a Cr–C–N film on bare SS316L by CUBMSIP. The result showed that the ICR of Cr–C–N coating decreased to 2.64 mΩ cm^{-2} at 140 N cm^{-2}. Meanwhile the cathode passivation current density was only 0.61 μA cm^{-2} at 0.6 V. Su JH et al. [38] prepared Cr–Mo–N coatings on SKD11 by hybrid PVD consisting of arc ion plating and unbalanced magnetron sputtering to investigate microstructure and phase evolution of CrMoN coated samples. Mo element can improve the anti-pitting corrosion of stainless steel [39,40]. Molybdenum nitrides have been investigated as an anode for micro-supercapacitors [41]. Wang L X et al. [42] prepared molybdenum nitrides diffusion coating on SS304L by plasma surface diffusion alloying method. The result showed that the I_{corr} of coatings were 4.97 μA cm^{-2} (anode) and 3.83 μA cm^{-2} (cathode) respectively. Zang et al. [43] deposited Ti–Mo–N on SS316L by arc ion plating. Although the corrosion resistance of Ti–Mo–N coatings is lower than single TiN film also higher than bare SS316L. However previous studies on Mo element mostly concentrate on mechanical properties. So the main purpose of this paper is to study surface morphology, corrosion resistance, electrical conductivity and corrosion mechanism of CrMoN films with various Mo contents. It is expected to improve the corrosion resistance of SS316L as bipolar plate for PEMFCs.

Experimental

Deposition process

SS316L was selected as the substrate of bipolar plate for PEMFCs. The element and content of SS316L are shown in Table 1. The dimension of substrate is 20 mm × 20 mm × 3 mm. The substrate was polished by SiC abrasive paper with #400.800.1200.1500.2000 grits, and 0.5 μm diamond paste. After polished, the sample was ultrasonically cleaned with acetone, alcohol and deionized water for 20 min respectively, then dried with air.

The deposition process was accomplished by CEUBMSIP (Teer UDP 650 coating systems). Two high purity Cr targets and one Mo target were selected as sputtering source. The samples were fixed on a rotatable substrate holder. Before deposition, the chamber was first keep at base pressure at 2.5 × 10^{-5} torr. Fig. 1 shows the academic diagram of CrMoN coatings. Ar (99.99%) was chosen as sputtering gas. Initially, the samples were cleaned by plasma sputtering for 30 min with a 0.3A applied current of targets to remove oxides. Then increased the current of Cr target from 0.3A to 4A to deposit Cr layer which can improve the adhesive between coating and substrate. Thirdly, CrN layer was deposited by bubbling nitrogen. The current of Mo target was changed from 0A to 6A to fabricate the CrMoN coated samples with different Mo content.

Characterization of coating

The phase structure of samples was analyzed by X-ray diffractometer using Cu Kα radiation operated at 40 KV and 100 mA, and the scan rate of (2θ) is from 20° to 80°. Surface morphology of samples was observed by a field scanning electron microscopy (FE-SEM). The hardness of the coated samples were measured by nano-indentation (Nano Indenter G200).

Interfacial contact resistance

Wang's method was used to measure the ICR between the coated sample and gas diffusion layer (GDL) [44]. As shown in Fig. 2(a), two pieces of carbon papers were sandwiched between the two Au-coated copper plates and samples. A constant current (5A) was applied to the coated samples through

Table 1 – Chemical compositions of the bare SS316L sample.

Cr	Ni	Mo	Mn	Si	P	C	S
20.0–21.0	6.0–7.0	1.5	1.5	1.0	0.04	0.03	0.03

Please cite this article in press as: Jin J, et al., Effects of Mo content on the interfacial contact resistance and corrosion properties of CrN coatings on SS316L as bipolar plates in simulated PEMFCs environment, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.04.044