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Short communication

Achieving ultrahigh corrosion resistance and conductive zirconium oxynitride coating on metal bipolar plates by plasma enhanced atomic layer deposition

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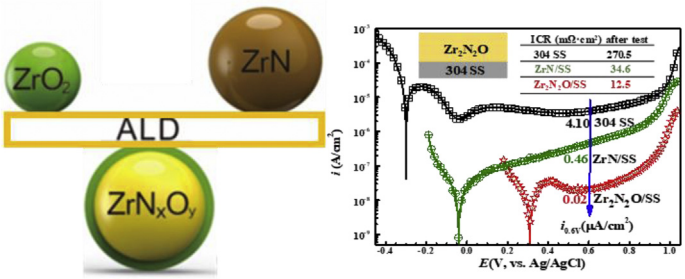
HIGHLIGHTS

- A controlled amount of oxygen is incorporated into ZrN by plasma enhanced ALD.
- Zr_2N_2O exhibits ultrahigh corrosion resistance in simulated PEMFCs.
- Zr_2N_2O combines the high corrosion resistance of ZrO_2 and high conductivity of ZrN.
- Zr_2N_2O possess lower interfacial contact resistance than ZrN after the tests.

GRAPHICAL ABSTRACT



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ABSTRACT

Susceptibility to corrosion of metal bipolar plates limits their application in polymer electrolyte membrane fuel cells (PEMFCs) and hence, the development of a conductive coating with high corrosion resistance is essential. Zirconium nitride (ZrN) exhibits high corrosion resistance but the interfacial contact resistance (ICR) after the long-term test is not satisfied owing to the surface oxidation and the corrosion products. To further improve the corrosion resistance and retain a considerable electrical conductivity, herein, we present a novel zirconium oxynitride (Zr_2N_2O) coating on 304 stainless steel by incorporating a controlled amount of oxygen into ZrN with plasma enhanced atomic layer deposition. The corrosion current density of the Zr_2N_2O coated specimen is found to be over one order of magnitude lower than that of the ZrN coated substrate. More importantly, after the long-term test, the ICR of Zr_2N_2O coated specimen is much smaller than that of ZrN coated specimen owing to the improved oxidation resistance and decreased corrosion rate, suggesting incorporating a controlled amount of oxygen into conductive coating is a feasible strategy to achieve an ultrahigh corrosion resistance while retaining a considerable electrical conductivity.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered as a promising technology for automotive applications and portable devices [1]. Bipolar plates, as a key component of PEMFCs, play a critical role in conducting electrons to adjoining cells, supporting the membrane electrode assembly and facilitating the removal of heat and reaction products [2]. Therefore, the bipolar plates are expected to exhibit high corrosion resistance, low interfacial electrical resistivity, low gas permeability, good mechanical strength and high chemical

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stability under PEMFCs working conditions [3]. Presently, carbon-based bipolar plates are widely used but the poor mechanical properties significantly limit its application, particularly in automobiles or other devices that involve mechanical vibration during their operations [4]. In this respect, stainless steel is considered as an attractive candidate material for metal bipolar plates. Nevertheless, stainless steel is susceptible to corrosion under harsh acidic (pH 2–5) condition in PEMFCs [5], and the subsequently formed corrosion products on the stainless steel surface greatly increase the interfacial contact resistance (ICR) and eventually lead to the poor stack performance [5]. Hence, an electrical conductive coating with high corrosion resistance is very much desired to enable its application as metal bipolar plates. To improve its corrosion resistance and decrease its ICR, various types of coating materials, such as transition metal nitrides including ZrN, TiN and TaN, have been applied on the metal surface [6–8]. Although transition metal nitrides coated stainless steel offers an improved corrosion resistance, its high corrosion current densities in the range of 10^{-6} to 10^{-5} A/cm^2 still makes it not suitable as metal bipolar plates [6–8].

Zirconium oxynitride (ZrN_xO_y) has a high resistance to dissolution in acidic media of PEMFCs, and has been studied as a catalyst for oxygen reduction reaction [9]. Notably, electrical conductivity of ZrN_xO_y varies from conducting ZrN to insulating ZrO_2 when the content of oxygen in ZrN_xO_y increases [10]. This dependence of electrical conductivity of ZrN_xO_y on oxygen content enables the application of oxygen plasma enhanced atomic layer deposition (PEALD) through controlling the oxygen content in ZrN_xO_y by adjusting the duration of oxygen plasma, a remarkable and highly desired deposition technique [11]. Therefore, a ZrN_xO_y coating fabricated by incorporating small amount of oxygen atoms into the ZrN holds the potential to achieve a comparable electrical conductivity and enhanced corrosion resistance simultaneously. In this study, a ZrN_xO_y coating was deposited on 304 SS metal substrate through PEALD and a 36 nm thin film of single phase Zr_2N_2O (confirmed by XRD and TEM) was obtained. The electrochemical behaviors, ICR and long-term stability were investigated, the corrosion current density of the ZrN_xO_y coated substrate was found to be over two orders of magnitude lower than that of the bare substrate while retaining considerable electrical conductivity.

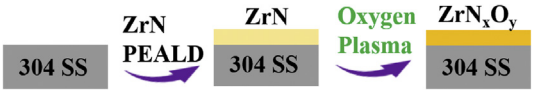
2. Experimental details

2.1. Material and solution

The substrate material was 304 SS with nominal chemical composition (in at. %) of 0.072C, 1.43 Mn, 0.57 Si, 18.24 Cr, 8.06 Ni, 0.07 Cu, 0.048 P, 0.0088 S, and Fe for the balance. The size of the specimen was 12 mm × 12 mm × 2 mm. All of the specimens were first ground up to 1200# SiC paper, and then successively cleaned with distilled water, rinsed with alcohol and dried up in air. The test solution was 0.5 M H_2SO_4 + 2 ppm NaF to simulate the working condition of PEMFC. Prior to and during the electrochemical measurements, the solution was purged with air. Multiple electrochemical experiments and ICR measurements were conducted on separate specimens to ensure reproductivity of the results reported in this work.

2.2. Coating deposition process

ZrN_xO_y coatings on 304 SS substrate were grown in a continuous flow reactor ALD-150LX (Kurt J. Lesker) equipped with an inductively coupled (0.6 kW and 13.56 MHz) remote-plasma (ICP) source. ZrN_xO_y film was obtained from PEALD grown ZrN upon exposure to Oxygen ICP plasma. ZrN films were grown using tetrakis dimethyllamino zirconium (TDMAZr) precursor and forming gas (5% H2, 95% N2) ICP plasma using deposition cycles parameters as 0.10 s TDMSZr pulse/12 s purge/9 s forming gas ICP plasma/9 s purge as reported in literature [12]. To ensure uniform oxidation, after every 5 nm thick deposition, ZrN film was exposed to oxygen plasma for 50 s, and this deposition/oxidation sequence is illustrated in Scheme 1.



Scheme 1. Deposition process of ZrN_xO_y coating.

2.3. Electrochemical measurements

A Solartron electrochemical workstation was used to perform the potentiodynamic polarization tests. An Ag/AgCl electrode (4.0 M KCl solution) connected to a salt bridge acted as the reference electrode and a platinum mesh as the counter electrode. For the bare specimen, prior to the tests, the working electrode was initially potentiostatic polarized at −0.8 V (all reported potential are based on Ag/AgCl) for 10 min to remove the native oxide layer on the surface. When the open circuit potential (OCP) reached a stable state, potentiodynamic polarization curves were measured at a scan rate of 1 mV/s from an initial potential of −0.3 V vs. OCP to transpassive potential region. Potentiostatic polarization measurements were intermittently carried out for 42 h (6 h every day for a week) at +0.6 V. EIS measurements were conducted at OCP with an amplitude of AC signal of 10 mV and the frequency was swept from 100 kHz to 10 mHz. All the tests were done at ambient temperature.

2.4. Coating characterization

ZrN_xO_y coating was characterized using glacing incidence X-ray diffraction (XRD) measurements at an incidence angle of 0.5°. Cross-sectional analyses in transmission modes were carried out on a lamella prepared by focused ion beam (FIB) system using the “in situ” lift-out technique. The samples were then examined by scanning transmission electron microscope (STEM) to obtain the cross-sectional image and elements distribution. The compositions of coating were analyzed by XPS with a monochromatic Al Kα radiation source and a hemispherical electron analyzer operating at a pass energy of 1486.6 eV. No sputtering was conducted before the analysis. The C1s peak at 284.8 eV was chosen as the calibration peak. The XPS data were fitted by CasaXPS v.2.3 with an iterated Shirley background. The Fermi level electronic structures of ZrN_xO_y, ZrN, and ZrO_2 coatings were analyzed from valence band-XPS spectrum measured using Axis Ultra Spectrometer (140 W, 1486.6 eV Al Ka source) from Kratos Analytical.

2.5. Interfacial contact resistance measurement

The interfacial contact resistance (ICR) between the specimens and carbon paper was determined using methods described elsewhere [2,5]. In details, two pieces of conductive carbon papers were sandwiched between the specimens and two copper plates (both sides are plated with gold to increase the conductivity). A constant electrical current was applied via the two copper plates and the variation of the total resistance was recorded as a function of steadily increasing compaction force from 60 to 240 N/cm^2. The ICRs of the specimen before and after the polarization tests were both measured, and the typical results at the compact force of 140 N/cm^2 were reported in this work.

3. Results and discussion

ZrN_xO_y coating is obtained through oxygen plasma treated ZrN by PEALD (Scheme 1). The XRD pattern in Fig. 1a shows a single phase and matches well with Zr_2N_2O (PDF-#50–1170). The cross-section TEM image (Fig. 1b) exhibits a d-spacing of 0.2963 nm (Fig. 1c), which corresponds to the value calculated from the XRD pattern of Zr_2N_2O at the (222) plane [13]. The EDS elemental mappings (Fig. 1d) presents the homogeneous distribution of N and O throughout the cross-section,