



Corrosion behaviour of austenitic stainless steel as a function of methanol concentration for direct methanol fuel cell bipolar plate



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HIGHLIGHTS

- Corrosion behaviour of AISI 304 stainless steel in DMFC anodic environment as a function of methanol concentrations.
- Electrochemical tests show that methanol decreases the corrosion rate of 304 SS.
- Passive film formed on 304 SS has a duplex electronic structure.
- The passive film is composed of an external n-type and an internal p-type semiconductor layer.
- The increase of methanol concentration decreases the surface conductivity of 304 SS.

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ABSTRACT

The corrosion behaviour of an AISI 304 stainless steel (304 SS) is investigated in aqueous acid methanol solutions (0.5 M H₂SO₄ + 2 ppm HF + x M CH₃OH, x = 0, 1, 5, 10 and 20) at 50 °C to simulate the varied anodic operating conditions of direct methanol fuel cells. Electrochemical measurements including potentiodynamic polarisation, potentiostatic polarisation and electrochemical impedance spectroscopy tests, are employed to analyse the corrosion behaviour. The results reveal that the corrosion resistance of 304 SS is enhanced in solutions with higher methanol content. Scanning electron microscopy and inductively coupled plasma atomic emission spectrometry data indicate that the surface corrosion on 304 SS is alleviated when the methanol concentration is increased. According to the X-ray photoelectron spectroscopy and Mott–Schottky analyses, the passive films formed on the 304 SS after potentiostatic tests in all the test solutions are composed of a duplex electronic structure with an external n-type semiconductor layer and an internal p-type semiconductor layer. Further analyses of the surface conductivity conducted by measuring the interfacial contact resistance between the 304 SS and carbon paper reveal that the passive film formed in the solution with higher methanol content exhibits lower conductivity.

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1. Introduction

Polymer electrolyte membrane fuel cells, which convert chemical energy into electric power via catalytically electrochemical reactions, have gained extensive attention as new power sources due to their relatively simple operating mechanisms, high efficiency and low emissions [1–4]. For portable applications of polymer electrolyte membrane fuel cells, there are two main choices of fuels: hydrogen and methanol. Hydrogen can be stored in forms of metal hydrides or compressed gases. The metal hydrides possess large specific weights, and the compressed gases occupy relatively large volumes. Moreover, the compressed gaseous hydrogen has

potential safety issues when used in most portable electronics. Compared to hydrogen, liquid methanol has greater volumetric and gravimetric energy density, making it much easier to store, transport and replenish. These advantages make direct methanol fuel cells (DMFCs) suitable for meeting the rapidly growing need for portable power sources in devices, such as mobile phones, notebooks, and portable electronic devices [5–8].

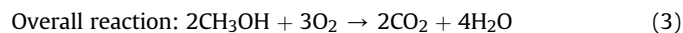
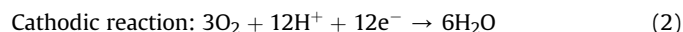
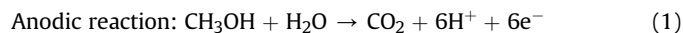
Bipolar plates are one of the most crucial components in the DMFC stack, constituting 80–85% of the total weight and 25–45% of the total cost of the fuel cell stack [9–11]. A bipolar plate physically separates the individual cells in the stack, electrically connects cell units and uniformly distributes the fuel and oxidant gas over the electrode reaction surface. Various materials have been screened as bipolar plates in recent years. Stainless steels are potential candidates for bipolar plate materials due to their good electrochemical

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stability, high levels of electrical and thermal conductivity as well as good machinability.

During DMFC operation, the electrochemical reactions involved are expressed as follows [12,13]:



Both the performance and the efficiency of the DMFC are strongly influenced by the methanol concentration due to methanol crossover. The DMFC usually shows a higher power density when fed with lower concentrations of methanol solutions (1–4 M) [7,14–17]. Nevertheless, a more concentrated methanol solution helps enhance the specific weight energy density of the DMFC system. More concentrated methanol solutions can be utilised by modifying existing membranes or employing components that prevent methanol crossover [18–20]. Furthermore, during fuel cell operation ions such as H^+ , SO_4^{2-} and F^- can be released from the perfluorosulphonic acid membrane [21,22]. Therefore, according to the above description, the bipolar plates are exposed to aqueous solutions containing acid and methanol. As previously reported [23,24], the corrosion behaviour of stainless steel in organic solvents is different from that in aqueous solutions, due to differences in the electric and binding interactions between the metal and solvent as well as in the physicochemical properties such as the dielectric constant, viscosity and solubility of the reactants or products. The corrosion behaviour of stainless steel in non-aqueous methanol solutions has been extensively studied based on the effect of a small amount of water (typically less than 0.1 wt%) on corrosion, passivation and pitting processes [24–28]. However, the influence of methanol concentration on the corrosion behaviour of stainless steel-based bipolar plates in acidic aqueous solutions is not yet completely understood. Therefore, in this paper, the corrosion performance and the surface conductivity of an austenitic stainless steel AISI 304 were investigated using an aqueous acid methanol solution ($0.5 \text{ M H}_2\text{SO}_4 + 2 \text{ ppm HF} + x \text{ M CH}_3\text{OH}$, $x = 0, 1, 5, 10$, and 20) while varying the methanol concentration to simulate the varied anodic operating conditions of DMFCs. The primary aim of this work is to offer fundamental information regarding the research and development of stainless steel bipolar plates for DMFCs.

2. Experimental section

2.1. Sample preparation

In this work, an austenitic stainless steel (AISI 304) was chosen as metal bipolar plates for DMFCs. The nominal compositions of the applied AISI 304 stainless steel (304 SS) are presented in Table 1. Stainless steel sheets with thickness of 1.5 mm were cut into $10 \text{ mm} \times 10 \text{ mm}$ samples (with an area of 1 cm^2). Afterwards, the samples were ground with #360, #500, #800, #1000 and #1500 grit silicon carbide abrasive papers, polished mechanically with

$0.25 \text{ }\mu\text{m}$ alumina paste, rinsed with acetone in an ultrasonic cleaner, and dried at room temperature.

2.2. Electrochemical measurements

Solutions of $0.5 \text{ M H}_2\text{SO}_4 + 2 \text{ ppm HF} + x \text{ M CH}_3\text{OH}$ ($x = 0, 1, 5, 10$ and 20) at $50 \text{ }^\circ\text{C}$ were utilised to examine the effect of methanol concentration on the corrosion behaviour of 304 SS under DMFC anodic operating conditions. The temperature of the electrochemical tests was maintained with an isothermal bath. The electrochemical experiments were performed using a computer-controlled CHI660C electrochemical workstation. A typical three-electrode system composed of a platinum sheet (as the auxiliary electrode), the 304 SS samples (as the working electrode), and a saturated calomel electrode (SCE, as the reference electrode) was used for the electrochemical measurements. All the potentials reported are relative to SCE unless otherwise specified. Before test, each sample was embedded in a polytetrafluoroethylene (PTFE) holder that accurately exposed the fixed surface of the sample to the corrosion solutions.

To evaluate the basic corrosion behaviour of the 304 SS in solutions of $0.5 \text{ M H}_2\text{SO}_4 + 2 \text{ ppm HF} + x \text{ M CH}_3\text{OH}$ ($x = 0, 1, 5, 10$ and 20), potentiodynamic polarisation measurements were carried out. At the beginning of potentiodynamic test, each sample was stabilised at an open circuit potential (OCP) for 30 min, then started potential sweep from -0.2 V vs OCP to 1.2 V at a scanning rate of 1 mV s^{-1} . To investigate the performance of 304 SS under DMFC anodic operation conditions, potentiostatic tests were performed. In these tests, the samples were also stabilised at OCP for 30 min, the potential of -0.1 V was then applied, and the current–time curves were recorded for 10 h. To quantify the dissolved metallic Fe, Ni, and Cr ions produced during the potentiostatic process, all the test solutions (approximately 100 ml for each test) were collected after the 10 h potentiostatic tests. Inductively coupled plasma atomic emission spectrometry (ICP–AES) (Optima 2000 DV) was used to detect the Fe, Cr, and Ni ions dissolved in the collected solutions. After the 10 h potentiostatic tests, electrochemical impedance spectroscopy (EIS) was carried out over a frequency range from 100 kHz to 10 mHz with a potential amplitude of 10 mV. The impedance spectra were interpreted with an equivalent circuit that was used to fit the experimental EIS data. The process of fitting was carried out with a ZSimpWin software.

The semi-conductive properties of passive films formed on surface of stainless steel can be determined by the flat band potential E_{fb} and doping density extracted from Mott–Schottky plots. The Mott–Schottky analysis was carried out from -0.5 V to 0.2 V at a scanning rate of 50 mV per step with a frequency and an amplitude of 500 Hz and 5 mV, respectively.

2.3. Surface morphology and passive film analysis

After the 10 h potentiostatic tests in solutions of $0.5 \text{ M H}_2\text{SO}_4 + 2 \text{ ppm HF} + x \text{ M CH}_3\text{OH}$ ($x = 0, 1, 5, 10$ and 20), the surface morphology of the 304 SS samples was observed via scanning electron microscopy (SEM) (SUPRA 55 SAPPHIRE, ZEISS), and the composition of the passive film formed on the samples was identified qualitatively and quantitatively using X-ray photoelectron spectroscopy (XPS). The XPS analysis was carried out in an ESCALAB 250 electron spectrometer using an Al K α source (1486.8 eV). The depth profile was achieved by Ar etching with ion energy of 0.5 keV. The sputtering rate of the Ar-ion gun was determined to be approximately 0.06 nm s^{-1} under the applied conditions.

The interfacial contact resistance (ICR) was measured using the method proposed by Wang et al. [3], which was detailed in Refs. [4,11].

Table 1
Chemical composition of AISI 304 stainless steel (wt%).

| Metal | C | Cr | Ni | Si | S | P | Mn | Fe |
|--------|-------|-------|------|------|-------|-------|------|---------|
| 304 SS | 0.049 | 18.20 | 8.66 | 0.58 | 0.007 | 0.021 | 1.05 | Balance |

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