

CORROSION RESISTANCE OF 316L STAINLESS STEEL IN FUEL CELL ELECTROLYTE

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The corrosion resistance and semiconductors of passivation film on the surface of 316L stainless steel has been explored using linear polarization, Potentiostatic polarization electrochemical impedance spectroscopy (EIS) and Mott – Schottky analysis in 0,1 / mol/L Na_2SO_4 and 0,01 / mol/L HCl solution in the steady state condition. Based on the Mott-Schottky analysis, the density and thickness of the passivation film are related to the potential formed by the passivation film. The passivation film is an n-type semiconductor. There is no metal ion loss or cation vacancy remaining; when the film forming potential is 0,3 / V, The chemical reaction rate at the interface is slow, and the passivation film is denser than the passivation film formed at other potentials.

Key words: 316L stainless steel, corrosion, polarization, electrolyte, potential

INTRODUCTION

With the rapid development of the global economy and society, energy consumption is also increasing [1]. The bipolar plate is the key component of the battery stack made up of PEMFC single cells in series. The PEMFC bipolar plate working medium is generally an acidic environment with a pH of 3 to 5. The contains a certain amount of SO_4^{2-} , F^- and a relatively small amount of NO_3^- , Cl^- and others ions when the battery is in operation. Corrosion resistance of stainless steel in PEMFC environment can not meet the needs of long-term stable operation of fuel cells, and its surface passivation can also lead to increased contact resistance between the bipolar plates and the membrane electrode diffusion layers [2,3], thereby reducing the fuel cell output power.

The coating on the stainless steel surface must not only have good corrosion resistance and electrical conductivity, but also have a good combination with the base alloy. Although the research on fuel cell bipolar plates is very comprehensive [4-7], the research on the density and diffusion of point defects in the fuel cell electrolyte of passivation films is seldom involved [8,9]. In this work, electrochemical impedance spectroscopy and Mott-Schottky analysis of 316L stainless steel have been performed. The potential method was polarized at different film forming potentials for 1 / h. The passivation film was electrochemically examined to investigate the corrosion resistance and semiconductor behavior of the passive film.

EXPERIMENTAL METHODS

In this paper, 316L stainless steel was used as the sample. Composition of steel: C is 0,021 / %, Si is 0,56 / %, Mn is 1,33 / %, P is 0,031 / %, Cr is 17,34 / %, Ni is 10,19 / %, Mo is 2,01 / %, N is 0,022 / %.

In this experiment, the corrosion resistance of the samples was measured by Autolab electrochemical workstation. The potentiostatic polarization, Electrochemical impedance spectroscopy, and Mott-Schottky curves of the samples were measured using the corresponding test software. Three-electrode system was used in the experiment. The saturated calomel electrode was used as the reference electrode. The platinum plate was used as the auxiliary electrode. The sample to be tested was 316L stainless steel, and the experiment temperature is 60 / °C. The solution (0,1 / mol/L Na_2SO_4 and 0,01 / mol/L HCl) was prepared from analytical grade Na_2SO_4 , HCl and distilled water.

The working electrode was polarized at -1,2 / V for 3 / min before the test to remove the oxide film formed on the surface of the 316L stainless steel under long-term air conditions. According to the result of polarization curve, 316L stainless steel was poled at 0 / V, 0,1 / V, 0,2 / V, 0,3 / V, and 0,4 / V potential for 1 / h to form a passivation film on the surface. Then the passive film was subjected to an impedance test. The test frequency was from 100 / kHz to 10 / mHz, and the test was performed at the self-corrosion potential. The Mott-Schottky experiments were done by measuring the frequency response at 1 kHz scan from -0,4 / V to 0,6 / V. The polarization curve was done by measuring during a scan rate of 5 / mV/s from -2 / V to 2 / V.

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RESULTS AND DISCUSSION

Electrochemical corrosion testing

As shown in Figure 1, after a certain period of time, the corrosion current density tends to be flat and stable within a certain range. After the passivation film is fully formed, the corrosion current density is stable, and the growth and dissolution of the passivation film also maintain a dynamic balance. With the passage of time, the passivation film is stable.

It can be seen in the Figure 2 that in the high frequency region, each impedance is composed of impedance arcs. These semi-circular arcs are not standard semi-circular shapes but are slightly “squashed”, indicating that the control step is still a charge transfer step and has only one time constant. When the filming potential is 0,3 / V, the impedance modulus $|Z|$ is the largest, and the stainless steel has the strongest corrosion resistance.

From the Figure 3 diagram, it can be seen that when the filming potential is 0,3 / V, the impedance modulus $|Z|$ is always higher than the other three conditions in the high and low frequency regions. From the Figure 4 diagram, it can be seen that the maximum phase angle

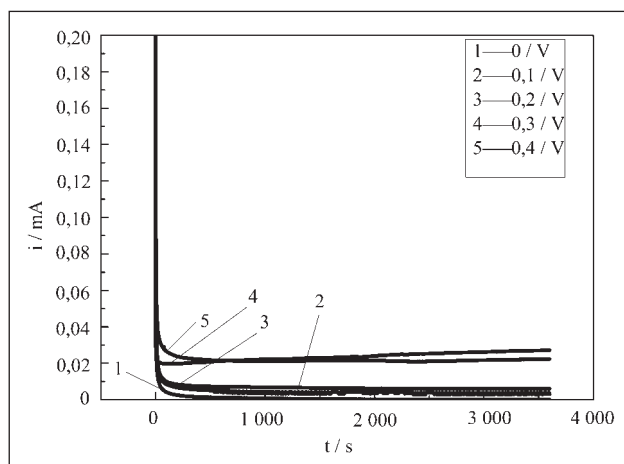


Figure 1 Potentiostatic polarization 1h at different film forming potential for 316L stainless steel

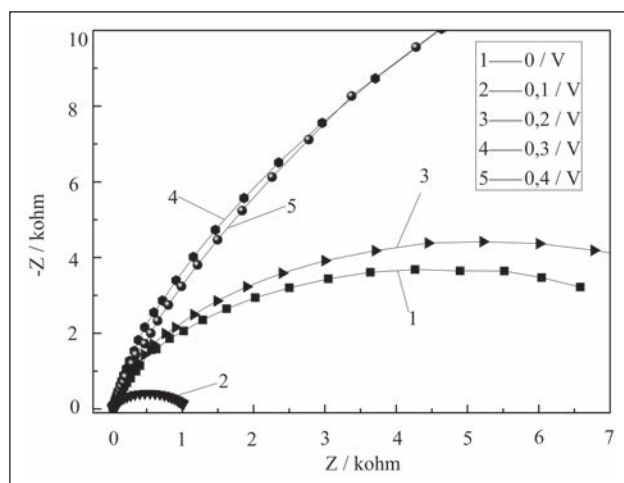


Figure 2 Impedance spectra of 316L stainless steel at different film forming potentials

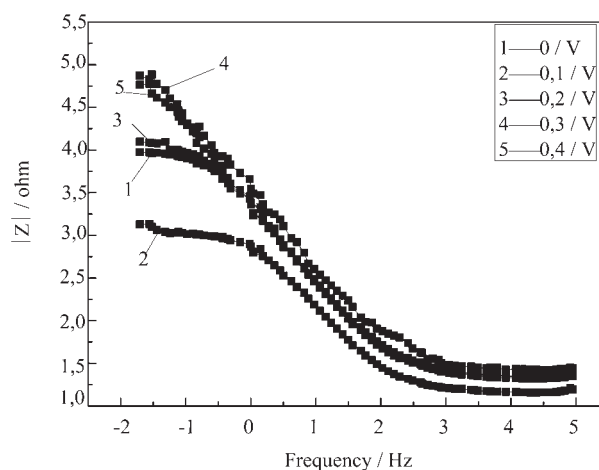


Figure 3 Bode diagram of 316l stainless steel at different film forming potentials (relationship between $|Z|$ and frequency)

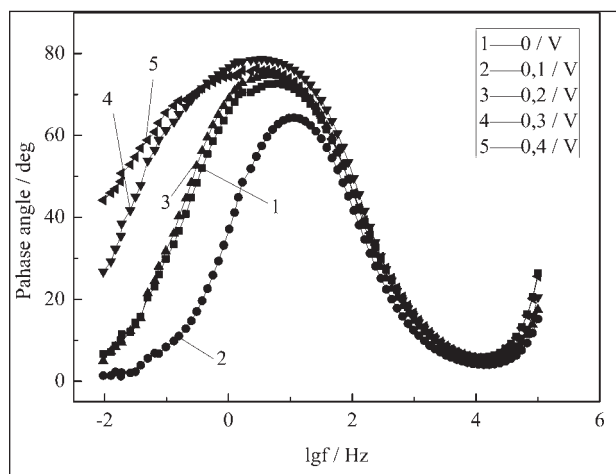


Figure 4 Bode diagram of 316l stainless steel at different film forming potential (relationship between phase angle and frequency)

at the filming potential of 0,3 / V is slightly larger, and the frequency at the maximum phase angle is lower than in other cases. Both the phase angle and the frequency curve consist of one crest and one trough, indicating that there is only one time constant.

Mott-Schottky analysis

The above analysis shows that the stability and compactness of the passivation film in 316L stainless steel are best when the filming potential is 0,3 / V and the polarization is 1 / h. These differences are related to the semiconductor properties of the passivation film. When the 316L stainless steel solution is contacted, the interface between the stainless steel surface and the solution forms a spatial double layer structure. The excess charge of the membrane will be distributed in the space charge layer, and the space charge layer will display consumption. As soon as possible, the functional relationship between the capacitance C of the space charge layer and the potential E can be expressed by the Mott-Schottky equation. The formula of the Mott-Schottky analysis is:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 e N_A} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (1)$$

When the passivation film is a p-type semiconductor, the relationship between C and E is as follows:

$$\frac{1}{C^2} = -\frac{2}{\epsilon\epsilon_0 e N_A} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (2)$$

In the formula, ϵ_0 is the permittivity of the vacuum ($8,85419 \times 10^{-12}$ / F/m), ϵ is the relative permittivity, and its value is calculated by taking the relative permittivity of the bulk oxide corresponding to the component in the passivation film as an approximation. Calculation, take 15 here. N_A and N_D are donor density and acceptor density, E_{fb} is flat band potential, E is electrode potential, k is Boltzmann constant ($1,38 \times 10^{-23}$ / J/K), T is thermodynamic temperature (K), and e is electron power ($1,6 \times 10^{-19}$ / C), KT/e is approximately 25 / mV and is negligible. Acceptor density and donor density can be obtained from the slope of the line drawn in the figure, Mott-Schottky.

Figure 5 shows the Mott-Schottky curve of stainless steel at different film forming potentials. It can be seen from the figure that the slope of the curve is positive. It can be seen from the formula that the passivation film is an n-type semiconductor. As we know, The Stainless steel passivation film exhibits different semiconductor properties due to its defects. If the passivation film has metal ions missing or vacancies of cations remain, such a passivation film generally exhibits the characteristics of a p-type semiconductor, and the opposite is expressed as n-type characteristics.

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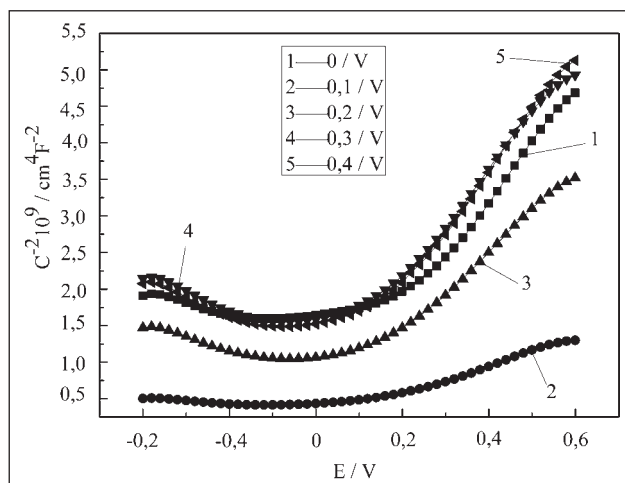


Figure 5 Mott-Schottky curve of passivation film at different film formation potentials

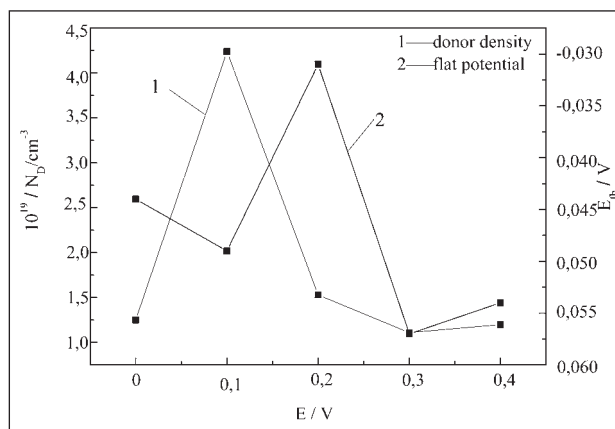


Figure 6 Relationship between film forming potential and donor density and potential with potential

of a p-type semiconductor, and the opposite is expressed as n-type characteristics.

It can be seen from the figure 6 that both the N_D and E_{fb} are at the minimum when the film forming potential is 0,3 / V. It can be seen that the interface has a slow chemical reaction rate, so the passivation film at 0,3 / V is denser than the passivation film at other potentials.

When the assumed capacitance corresponds to the space charge layer capacitance, the thickness of the space charge layer can be calculated using the following formula:

$$L = \sqrt{\left[\frac{2\epsilon\epsilon_0}{eN_D} \left(E - E_{fb} - \frac{KT}{e} \right) \right]} \quad (3)$$

Figure 7 shows the relationship between space charge layer thickness and film forming potential. In general, the thicker the space charge, the stronger the corrosion resistance of the passivation film. The figure shows that at 0,3 / V, the space charge layer is the thickest. That is to say, the corrosion resistance of the passivation film at 0,3 / V is the best, also confirmed the previous polarization curve and impedance conclusions, 316L stainless steel in the SO_4^{2-} , Cl⁻ solution in the 0,3 / V film forming potential The lower corrosion resistance

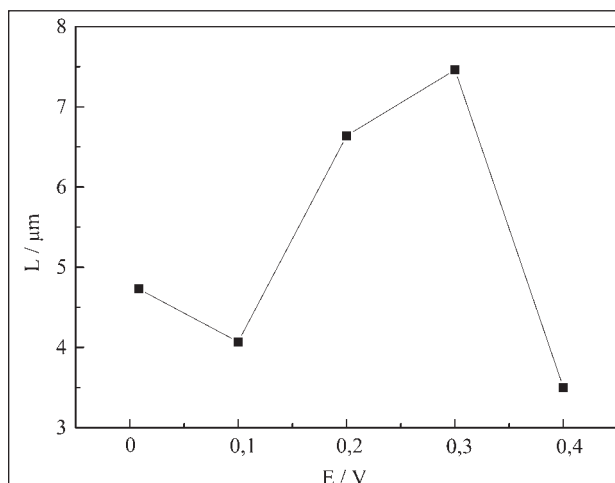


Figure 7 Relationship between space charge layer thickness and film forming potential

is better than the corrosion resistance at other deposition potentials.

CONCLUSION

The results of potentiostatic polarization test show that a dense and stable passivation film is formed on the surface of 316L stainless steel at each deposition potential. Polarization curve test shows that the corrosion current density is the smallest and the corrosion potential is relatively positive when the deposition potential is 0,3 / V. Electrochemical impedance test results show that when the film forming potential is 0,3 / V, the capacitive reactance in the impedance is higher than other film forming potentials; the Mott-Schottky curve test results show that the space charge layer thickness of stainless steel when the film forming potential is 0,3 / V Thicker, the same result as the above detection method.

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Note: The responsible translator for English is Yan Wu, University of Science and Technology Liaoning, Anshan, China.