

Corrosion of Stainless Steel Bipolar Plates in PEFC

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Stainless steels are one of the most promising materials as bipolar plates for polymer electrolyte membrane fuel cells (PEFCs). In use of stainless steel bipolar plates, however, corrosion and corrosion induced degradation of cell performance are anticipated. In the present study, corrosion behavior of SUS 304 and 310S stainless steels was investigated through polarization tests in the simulated PEFC environment (0.05M Na₂SO₄ (pH 2.3) + 2 ppm F⁻ solution at 353 K), contact resistance measurement between steels and carbon diffusion layer and cell operation. XPS analysis was also carried out to compare the steel surfaces after polarization measurements and cell operation. The results indicated that passive current density for SUS 310S stainless steel in the simulated PEFC environments was lower than that for SUS 304 stainless steel, as expected from higher Cr content. Longer polarization of these steels decreased the passive current density but increased contact resistance due to thickening of the passive film. The cell voltage drops after 3.6×10^6 s operation were 14 mV for graphite, 22 mV for SUS 310S and 46 mV for SUS 304 steel. Apparent corrosion was recognized for SUS 304 stainless steel served for cathode.

Key words: bipolar plate, PEFC, stainless steel, corrosion

1. INTRODUCTION

Polymer electrolyte membrane fuel cells (PEFCs, also referred to as proton exchange membrane fuel cells, PEM) are one of the ideal power generating systems in terms of cleanliness and energy efficiency [1]. PEFCs are principally composed of a stack of membrane electrode assembly (MEA) and bipolar plates. Bipolar plates give pathways to gases and water throughout electrodes and electronic connections to electrode materials through gas diffusion layers. Therefore bipolar plates are made of electroconductive materials such as graphite or metals. Metals are less brittle, less gas-permeable and more machinable than graphite or carbon based composite materials [2]. Several authors have proposed the use of stainless steels as bipolar plates [3-11]. However, chemical stability of metals depends strongly on their environments. Corrosion of metallic bipolar plates deteriorates cell performance because corrosion products increase the contact resistance between the plates and diffusion layer. Furthermore dissolved metallic ions are known to degrade the performance of membrane [12]. Therefore corrosion of metallic bipolar plate is the critical issue in order to realize less expensive and more reliable stack. In the present study, the corrosion behavior of SUS 304 and 310S stainless steels was investigated through cell operation up to 1000 h. Electrochemical tests in a simulated PEFC environment were also carried out to compare the surface states.

2. EXPERIMENTAL

2.1 Materials

Two types of austenite stainless steels with different contents of chromium (18 mass % for SUS304 and 25 % for SUS310S) and nickel (9% for SUS304 and 19% for

SUS310S) were compared in this study. These stainless steels plates (2 mm thick) were machined into a square (20 x 20 mm) and mounted into epoxy resin for polarization tests. The surfaces were finished using diamond paste polisher of 6 μm and cleaned ultrasonically in hexane for 15 minutes.

2.2 Polarization tests

Polarization tests were carried out in a PTFE lined cell which was filled with 200 cm³ of 0.05M Na₂SO₄ (pH 2.3) + 2 ppm F⁻ solution saturated with either argon or air in order to simulate the PEFC environment. Some tests were made in solutions with different concentrations of fluoride. A reference electrode (SCE) was placed out of the water bath which kept the temperature of the cell 353 K. Potentials are indicated as measured against this SCE without any correction for the thermal junction potential. Test specimens were polarized to -500 mV (SCE) first to remove air-formed films and then in the anodic direction by 1 mV s⁻¹. Specimens were also polarized at constant potentials of -100 mV and +600 mV to follow the current up to 29 ks.

2.3 Contact resistance measurements

Contact resistance was evaluated as a function of applied force according to the four-terminal method between the specimen and carbon fiber cloth which works as a diffusion layer for reactant gases.

2.4 Bipolar plates

A plate of stainless steel (80 x 80 x 6 mm) was machined into a bipolar plate with serpentine flow field according to the NEDO report by JARI [13]. The electrode area was 50 x 50 mm. The surface was polished down to 2000 grit and degreased. No further

pretreatment was made for the bipolar plates.

2.5 Cell operation

A single cell was assembled from stainless steel bipolar plates and a commercially available MEA with compressive force of 150 N cm^{-2} . The single cell was operated at 348 K under ambient pressure. The reactant gases were fully humidified at 343 K. The utilization was 70 % for the fuel gas (H_2) and 40 % for air. The current density was 0.5 A cm^{-2} .

2.6 XPS analysis

After polarization tests or cell operation, the surfaces of the stainless steels were analyzed by XPS (ULVAC-PHI 5600).

3. RESULTS AND DISCUSSION

3.1 Polarization curves

Fig. 1 shows the polarization curves for two kinds of stainless steels in the simulated PEFC environment, i.e. $0.05\text{M Na}_2\text{SO}_4$ (pH 2.3) + 2 ppm F^- solution at 353 K. SUS304 stainless steel showed a little higher current density than SUS310S but the difference did not seem critical since both steel satisfied the generally required corrosion rate of $<16 \mu\text{A cm}^{-2}$ [2]. In order to distinguish the superiority of SUS 310S stainless steel, polarization tests were conducted in solutions with higher concentration of fluoride. Fig. 2 (a) shows the current density – time curves for SUS 304 stainless steel at +600 mV as a function of concentration of fluoride. Fig. 2 (b) reveals the results of the same tests for SUS 310S stainless steel. Critical difference was found when the concentration of fluoride was 500 ppm. The current density started increasing after 10 ks for SUS304 stainless steel while it continued to decrease up to 29 ks for SUS 310S stainless steel. The results of similar tests at -100 mV are shown in Fig. 3. The difference in anodic current density between SUS304 and SUS 310S stainless steels became more pronounced in the solution with 1000 ppm of fluoride. But the current densities did not turn increasing up to 29 ks at this potential.

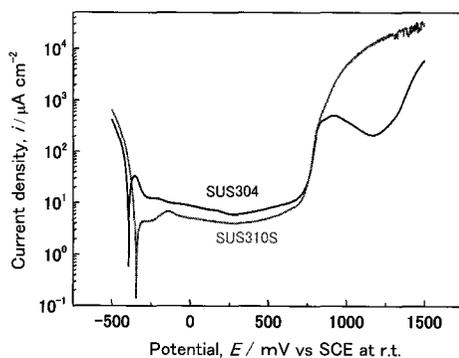


Fig.1 Anodic polarization curves for SUS 304 and 310S stainless steels in a deaerated $0.05\text{M Na}_2\text{SO}_4$ (pH 2.3) + 2 ppm F^- solution at 353 K.

3.2 Contact resistance

Fig. 4 shows the contact resistance between bipolar plate materials and carbon fiber cloth as a function of

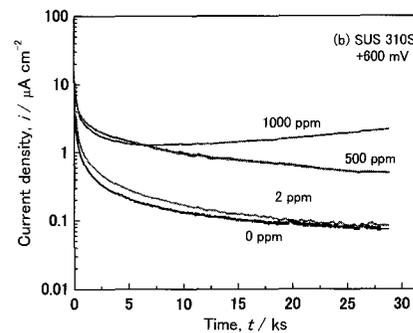
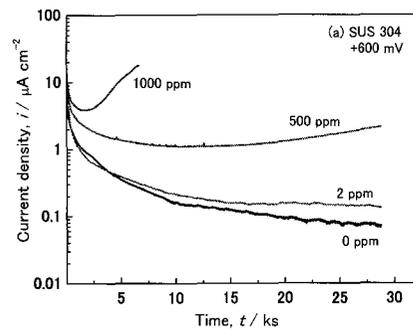


Fig. 2 Effect of concentration of fluoride on the time variation of anodic current density at +600 mV for (a) SUS 304 and (b) SUS 310S stainless steels in aerated $0.05\text{M Na}_2\text{SO}_4$ (pH 2.3) solutions at 353 K.

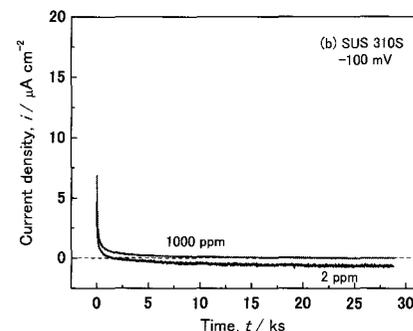
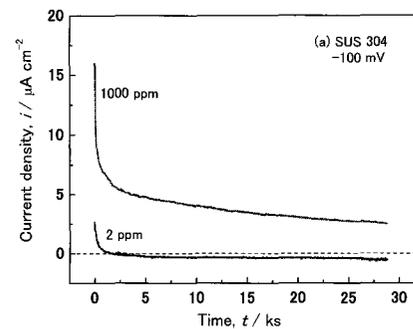


Fig. 3 Effect of concentration of fluoride on the time variation of anodic current density at -600 mV for (a) SUS 304 and (b) SUS 310S stainless steels in deaerated $0.05\text{M Na}_2\text{SO}_4$ (pH 2.3) solutions at 353 K.

applied pressure. The figure also includes the result for graphite. As expected, the resistance for graphite was small enough while stainless steels show about ten times larger value. Stainless steels after 29 ks polarization at -100 mV showed little increase in contact resistance but those at +600 mV showed about ten times increase. No apparent difference was found between SUS 304 and SUS310S stainless steels as for the contact resistance.

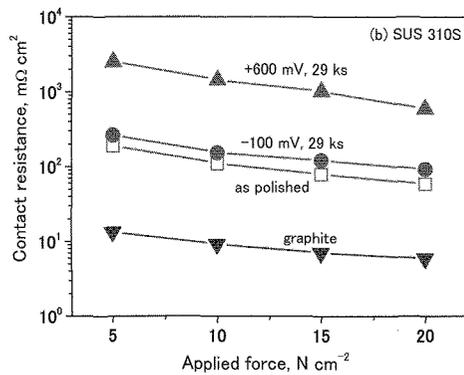
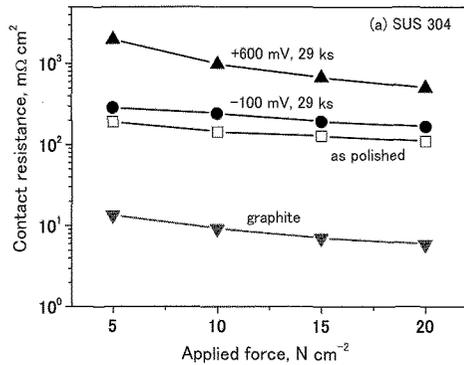


Fig. 4 Contact resistance between stainless steels and carbon fiber cloth after polarization for 29 ks in 0.05M Na₂SO₄ (pH 2.3) + 2 ppm F⁻ solution at 353 K.

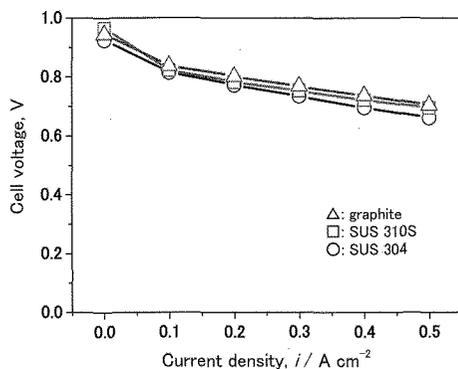


Fig. 5 Initial *i-V* characteristics of single cells using different materials for bipolar plates.

No apparent difference was found between SUS 304 and SUS310S stainless steels as for the contact resistance. Thus large potential drop was anticipated across the interface between stainless steel bipolar plates and gas diffusion layer.

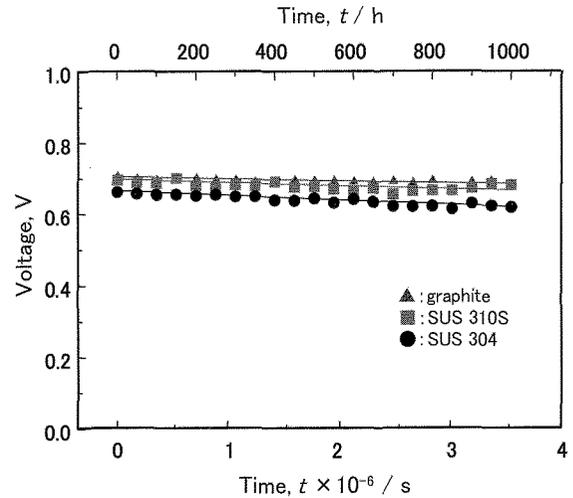


Fig. 6 The effect of materials for bipolar plates on the stability of cell voltage. Current density : 0.5 A cm⁻², Anode gas utility: 70%, Cathode gas utility : 40 %.

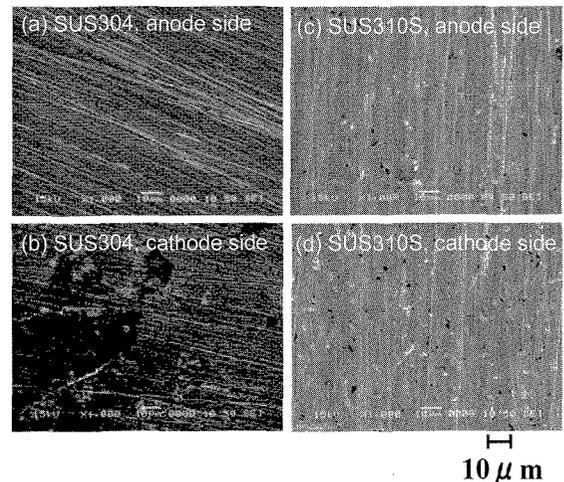


Fig. 7 Surface appearances of the rib surfaces of stainless steel bipolar plates after 3.6x10⁶ s operation.

3.3 Cell performance

The current – voltage characteristics at the beginning of operation of the single cells assembled with different materials of bipolar plates are shown in Fig. 5. The voltage drops for cells with stainless steel bipolar plates was not as large as anticipated from Fig. 4. The oxide films may be more conductive in a wet condition as in the PEFC environment. The cells were subjected to constant current load (0.5 A cm⁻²) for 3.6x10⁶ s. The time variations of the cell voltage are shown in Fig. 6. In the case of graphite bipolar plate, the voltage drop after 1000 h operation was as small as 14 mV. SUS310S stainless steel bipolar plate caused drop of 22 mV and no visible trace of corrosion was recognized. In case of SUS304 stainless steel, the voltage drop was as large as 46 mV. In Fig. 7, SEM pictures of the rib surfaces of the

Table 1 Cr/Fe atomic ratio in the films

Stainless steel	as polished	Polarization for 2.9×10^3 s		Cell operation for 3.6×10^6 s	
		-100 mV	+600 mV	anode	cathode
SUS 304	0.40	3.00	1.58	4.09	0.63
SUS 310S	0.60	1.97	2.51	12.57	7.81

bipolar plates after 3.6×10^6 s cell operations are shown. Apparent corrosion was recognized only on SUS304 stainless steel served for cathode.

3.4 Surface analysis

Fe2p spectra for SUS304 stainless steel after 2.9 ks polarization in 0.05M Na_2SO_4 (pH 2.3) + 2ppm F^- solution at 353 K and 3.6×10^6 s cell operation are shown in Fig. 8. After 3.6×10^6 s operation, the peak at 707 eV disappeared both from cathode and anode sides, indicating thickening of the oxide layer with progress of cell operation. The surface of the SUS 304 stainless steel bipolar plate used for cathode side was almost covered with iron oxide, as can be seen from Table 1 which summarized Cr/Fe ratio within each oxide layer. The results of XPS analysis for SUS 304 and SUS310S stainless steels after polarization tests in the simulated PEFC environments for 2.9 ks did not show distinct difference while those after 3.6×10^6 s cell operation indicated that surface oxide layer became more enriched with chromium for SUS 310S stainless steel.

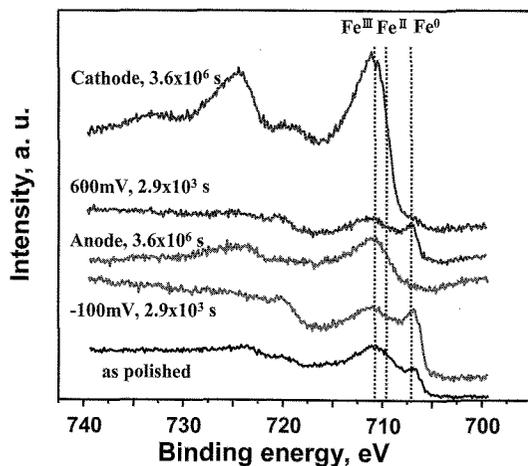


Fig. 8 Fe2p spectra of SUS 304 stainless steel after 2.9 ks polarization in 0.05M Na_2SO_4 (pH 2.3) + 2ppm F^- solution at 353 K and 3.6×10^6 s cell operation.

4. Conclusions

Two typical austenitic stainless steels, SUS 304 and 310S were evaluated as candidate materials for bipolar plates of PEFCs. The results of single cell operation up to 3.6×10^6 s revealed that SUS310S steel was chemically stable as a bipolar plate while SUS 304 steel suffered from general corrosion on the cathode side. Several electrochemical tests were also carried out for further characterization of these steels. Dynamic polarization

tests in the simulated PEFC environment were effective for ordering of materials: SUS 310S showed lower passive current than SUS 304 steel. But one could hardly conclude from only polarization curves if the material is chemically stable enough or not during long operation as a bipolar plate. Then current density – time curves were obtained as a function of concentration of fluoride. The increase in current density with concentration of fluoride was most remarkable for SUS 304 stainless steel polarized to +600 mV which is consistent with corrosion behavior of bipolar plates that SUS 304 stainless steel suffered from corrosion on the cathode side. Anodic polarization of these stainless steels to +600 mV in the simulated PEFC environment caused unfavorable increase in contact resistance against carbon diffusion layer. But cell voltage was not influenced so much as anticipated from contact resistance data. Passive films on stainless steels bipolar plates showing good cell performance were highly enriched with chromium while iron rich surface was recognized on corroded plate.

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