

Effect of Tantalum and Lanthanum Addition on Electrochemical Property of Austenitic Stainless Steel in a Simulated PEMFC Environment

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The electrochemical properties of W-modified austenitic stainless steels containing Ta and La were evaluated in a H₃PO₄ type PEMFC environment. Electrochemical test was conducted in 0.05 M H₃PO₄ solution at 80 °C and electrical property was conducted by contact resistance test. XPS was conducted to analyze the chemical elements consisting of passive film. Addition of La and Ta in W-modified austenitic stainless steel shows not only better corrosion resistance but also better electrical property.

Keywords : Bipolar plate; PEMFC; Austenitic stainless steel; W-modification; Ta and La addition

1. Introduction

Proton exchange membrane fuel cell (PEMFC) mainly consists of polymer electrolyte membrane, electrode and bipolar plate. The main function of bipolar plate is to provide electrical connection between the individual cells and to supply reactant gases separately. It also provide channel to remove product water. Graphite is widely used as a bipolar plate material of PEMFC due to its good corrosion resistance and high electric conductance. However, for commercialization of PEMFC, graphite bipolar plate has a limitation due to its high cost and bulky volume because of poor mechanical property and machining difficulty. In comparison to the graphite, metallic bipolar plate has various advantages. Among the metals, austenitic stainless steel is a possible alternative due to its good mechanical property and reasonably good corrosion resistance.¹⁾ However, metallic bipolar plate is very prone to corrosion in acidic and humid environment of PEMFC, and corrosion products on metal surface decrease power efficiency of PEMFC as well.

Currently, perfluorosulfonic acid (PFSA) polymer membranes (e.g. Nafion) are widely used as electrolyte of PEMFC. Nafion type PEMFC has some advantages. For example it is operated at low temperature and low temperature operation allows it to start quickly. However, this low operational temperature inherently results in serious

technical problems to be solved, including low cathode performance, difficult water management, high material cost for catalysts and low tolerance to fuel impurities, especially CO.^{2),3)} To solve this problem, PEMFC operation temperature should be increased above 100 °C. Then Nafion type electrolyte cannot be used in this temperature. To overcome this problem, phosphoric acid-type electrolyte has been suggested since it has high thermal stability and high proton conductivity. PEMFC with H₃PO₄-doped polybenzimidazoles (PBI) membranes can be operated at as high as 200 °C.⁴⁾

Our previous study has shown that addition of a proper amount of W to austenitic stainless steel improves both corrosion resistance and electric conductivity. To improve further such properties, we add La and Ta to W-modified austenitic stainless steel. In this paper, the effect of addition of Ta and La on the corrosion resistance and contact resistance of W-modified austenitic stainless steel was characterized with potentiodynamic polarization, potentiostatic polarization, and electrochemical impedance spectroscopy and contact resistance test. Auger electron spectroscopy was employed to understand the elemental distribution in the passive film and X-ray photoelectron spectroscopy was performed to analyze the chemical state of the elements consisting of the passive film.

2. Experimental

The experimental specimens are basically austenitic

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Table 1. Nominal composition of experimental stainless steel alloys (wt%)

Material	Cr	Ni	Mo	W	Ta	La	Fe
A	16.44	12.22	5.06				Bal.
B	17.89	11.77	1.97	3.23			Bal.
C	17.67	11.59	1.81	3.30	0.297	0.029	Bal.

stainless steel (18 Cr-12 Ni-4 Mo). Their chemical compositions are given in Table 1. To elucidate the effect of W, La and Ta on the corrosion and electrical properties, we modified alloy composition of Steel A by adding different amount of W, La and Ta. The stainless steel specimens were prepared using laboratory-scale vacuum arc melt furnace and homogenized at 1050 °C for 15 min, followed by water cooling.

Electrochemical polarization tests of both dynamic and static methods were employed to understand the electrochemical property of the experimental alloys in a PEMFC environment. The PEMFC environment used in this experiment was a simulated phosphoric acid type fuel cell electrolyte. Experiments were carried out in 0.05 M phosphoric acid (H_3PO_4) solution at 80 °C. The solution was bubbled with hydrogen gas and air to simulate anode and cathode environment, respectively, prior to and during the electrochemical experiment. Electrochemical experiments were used by three electrode system, with a carbon rod as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All specimens were polarized cathodically at $-0.7 V_{SCE}$ for 1 min to remove oxide on the specimen and stabilized at the open circuit potential (OCP) for 5 min. And then in potentiodynamic polarization test, specimens were polarized at a scanning rate of 0.5 mV/sec in a potential range from 0 V to 1.2 V with respect to the corrosion potential of each steel specimen. In potentiostatic polarization test, specimens were held at two potentials $-0.1 V_{SCE}$ and $0.6 V_{SCE}$ to simulate the PEMFC anode and cathode environment respectively. The current change was observed with time. After holding at $0.6 V_{SCE}$ for 1 hour, EIS test was conducted in a frequency range from 10000 Hz to 0.01 Hz with amplitude of 10 mV.

Contact resistance of the stainless steel specimens was evaluated by measuring voltage value when a current of 2A was applied to two copper end plates between which the stainless steel specimen was located. Compression force was applied from 30 N/cm² to 210 N/cm² using an Instron 4467.

XPS (X-ray photoelectron spectroscopy) was employed to analyze the chemical elements consisting of passive

film. To obtain information about chemical species through the depth of the passive film, specimens were sputtered at a 0.063 nm/sec with Al K α source (1486.8eV). XPS results were obtained to 10 level (sputtering for 10 sec/level). Binding energy of the elements was normalized by using binding energy of carbon, 285.6eV.

3. Result and discussion

Potentiodynamic polarization behaviors of experimental stainless steels in 0.05 M H_3PO_4 solution at 80 °C are displayed in Fig. 1. Fig 1 (a) and (b) show potentiodynamic polarization results in a simulated anode (air purge) and cathode (H_2 purge) condition, respectively. Polarization curves show a large stable passive region and transpassivity near oxygen evolution potential without any sign of pitting corrosion. Polarization curves show that all specimens do not have an active-passive transition region in 0.05 M H_3PO_4 solution at 80 °C because corrosion potential (E_{corr}) is formed at a passive region. Specimen A

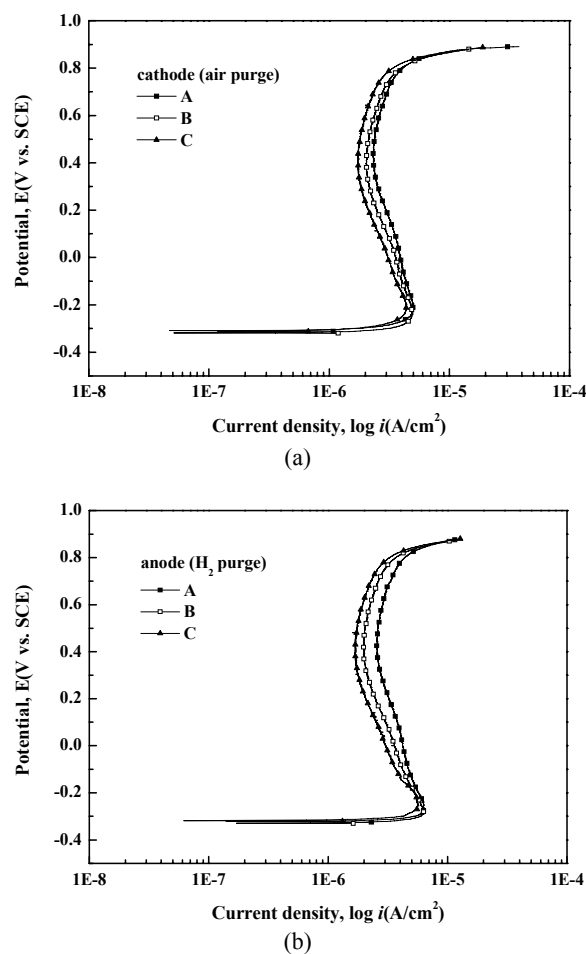


Fig. 1. Results of potentiodynamic test in 0.05 M H_3PO_4 solution at 80 °C with (a) air and (b) H_2 purge

is lower current density than specimen B and specimen C has the lowest current density in the passive region. Compared with current density in the passive region, polarization curve show that passive film of W-modified austenitic stainless steel is more stable than only Mo-added stainless steel and moreover passive film of La and Ta addition stainless steel is the most stable among the experimental specimens. The polarization behaviors at -0.1 V in anode condition and +0.6 V in cathode condition should be emphasized since PEMFC is operated at these two potentials. PEMFC operation potential of all specimens is located in the stable passive region. This means that austenitic stainless steel for bipolar plate can be protected by passive film in acidic environment of PEMFC. Potentiodynamic polarization test shows that substitution of W, addition of La and Ta to austenitic stainless steel gives rise to high corrosion resistance in a simulated PEMFC environment.

Potentiostatic polarization test was conducted to understand passivation characteristic for a long-term operation in a simulated PEMFC environment. Potentiostatic polarization curves are displayed in Fig. 2(a) and 2(b) in a simulated anode (air purge) and cathode (H₂ purge) condition, respectively. Current density of all specimens decreased rapidly at initial states and then is stabilized gradually. Local corrosion, such as pitting did not developed during the test. This means that the stability of passive film can well be maintained during long-term operation of PEMFC environment. Potentiostatic polarization test shows that substitution of W, addition of La and Ta to austenitic stainless steel provides better corrosion resistance in a simulated PEMFC environment.

EIS test was conducted to measure polarization resistance of passive film after passive film formed. Fig. 3 shows the impedance plots for specimens. All Nyquist plots are depressed semicircles different from ideal semicircles. In Bode plots, phase angle maximum value is smaller than 90° and absolute value of impedance slope is smaller than 1. It can be seen that formed passive film on experimental austenitic stainless steel is different from behavior of ideal capacitor. This is caused by surface roughness, local nonuniformity of dielectric material, porosity, mass transport effects and relaxation effects.⁵⁾ From EIS results, the equivalent circuit in Fig. 4 is proposed as a model for the interface of specimen and solution. R_s represents the electrolyte resistance, R_p represents the polarization resistance and Q represents the CPE (constant phase element). Table 2 gives the measured impedance parameters from proposed model. R_s of all specimens is similar since all test were conducted in a same solution. However, R_p as resistance against corrosion is different

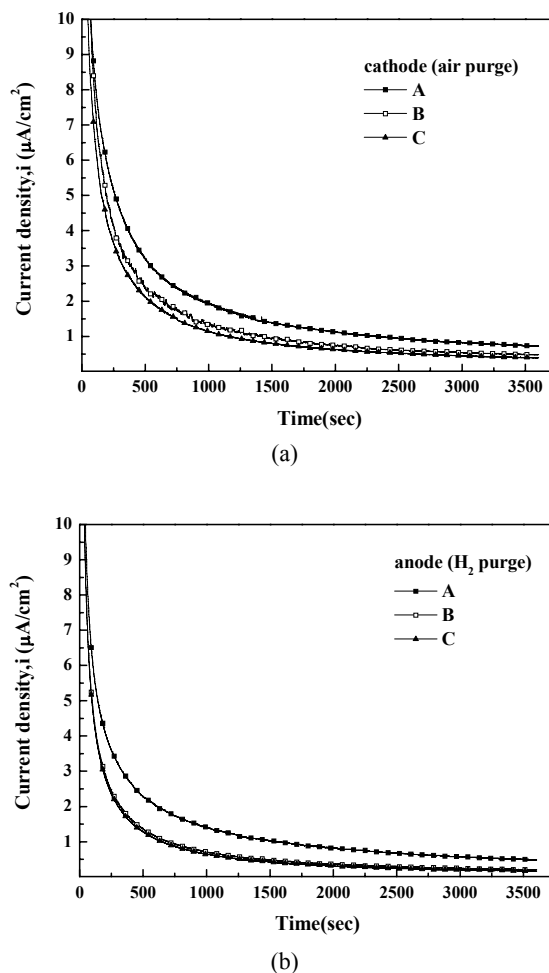


Fig. 2. Results of potentiostatic test in 0.05 M H₃PO₄ solution at 80°C with (a) air and (b) H₂ purge

among the specimens. R_p of specimen B is higher than specimen A and R_p of specimen C is the highest among the specimens.

Fig. 5 shows the contact resistance test results for the specimens. For contact resistance test, passive films were grown for 1 hour in a simulated air-purged cathode condition and H₂-purged anode condition. The contact resistance test was performed with applied pressure up to 210 N/cm² which was known as typical contact pressure applied to bipolar plate in PEMFC.¹⁾ Contact resistance decreases with increasing applied pressure and specimen C

Table 2. Equivalent circuit parameters

	R _s (Ωcm ²)	R _p (Ωcm ²)	Q(F)	α
A	32.65	3.106×10 ⁵	2.936×10 ⁻⁵	0.9333
B	28.45	3.637×10 ⁵	2.681×10 ⁻⁵	0.9359
C	28.84	4.047×10 ⁵	2.536×10 ⁻⁵	0.9306

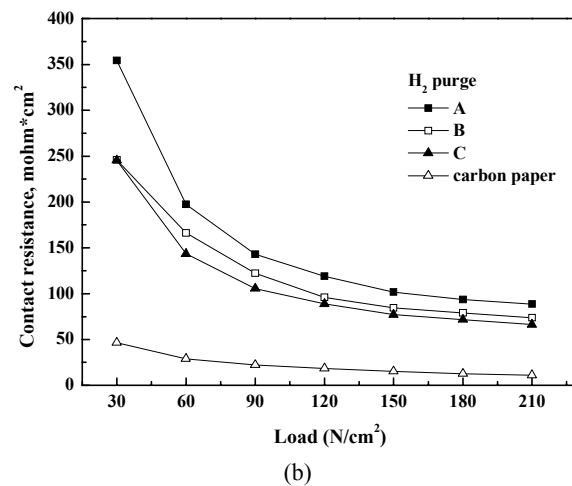
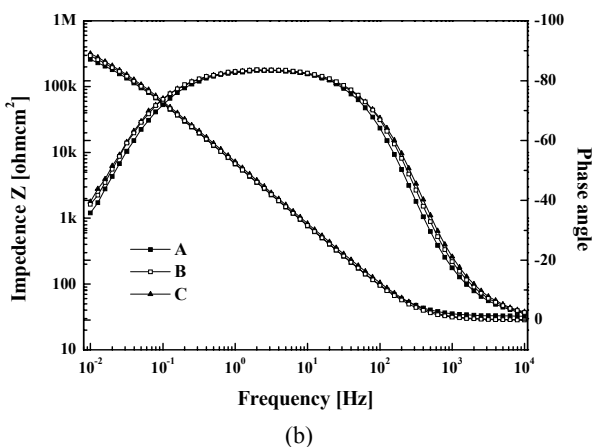
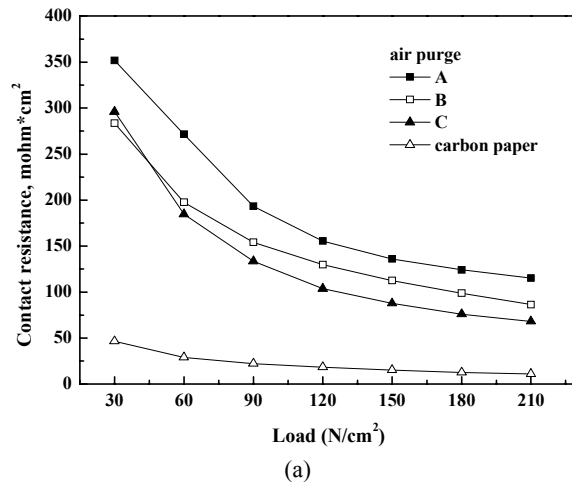
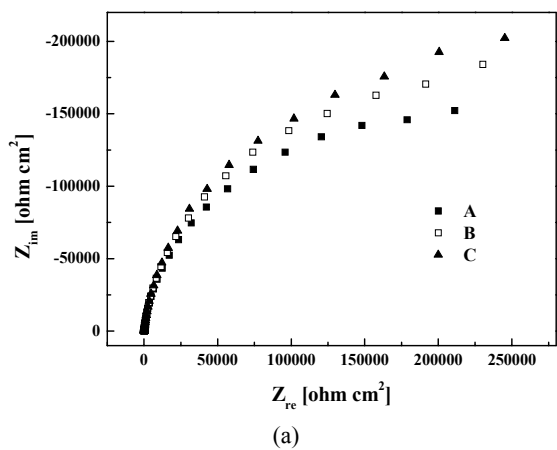


Fig. 3. Results of EIS test (a) Nyquist plot (b) Bode plot

Fig. 5. Contact resistance of specimens after postentostatic polarization test with (a) air and (b) H₂ purge

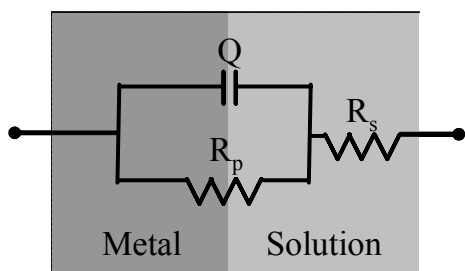


Fig. 4. Equivalent circuit model representing interface between passive film and electrolyte by the introduction of CPE concept.

is particularly the lowest value among the specimens. This means that substitution of W, addition of La and Ta shows not only better corrosion resistance but also lower contact resistance.

XPS analysis was conducted to understand the chemical state of the elements consisting of the passive film. Fig. 6 shows the XPS spectra of Ta for formed passive film on specimen C in 0.05 M H₃PO₄ at 80 °C. Fig. 5 indicates

that Ta 4f spectra of specimen C are metallic and oxidized state. Ta 4f electron peak of metallic Ta⁰ state was located at 21.9 eV and 23.8 eV and Ta 4f electron peak of oxidized Ta⁵⁺ state was located at 26.3 eV and 28.2 eV in the formed passive film of specimen C. This result indicates that addition of Ta to austenitic stainless steel forms Ta₂O₅ in the passive film and then high corrosion resistance is due to formation of Ta₂O₅ in a simulated PEMFC environment.

Fig. 7 and 8 show the XPS spectra of W for formed passive film on specimen B and C. W 4f electron peak of metallic W⁰ state was located at 30.9 eV and 33.1 eV and W 4f electron peak of W⁶⁺ state was located at 35.7 eV and 37.8 eV and W 4f electron peak of W⁵⁺ state was located at 34.7 eV and 36.8 eV in the formed passive film of specimen B and C. Generally, W was known as W⁶⁺ in the passive film of stainless steel. However, oxidation state of W in the passive film of specimen B and

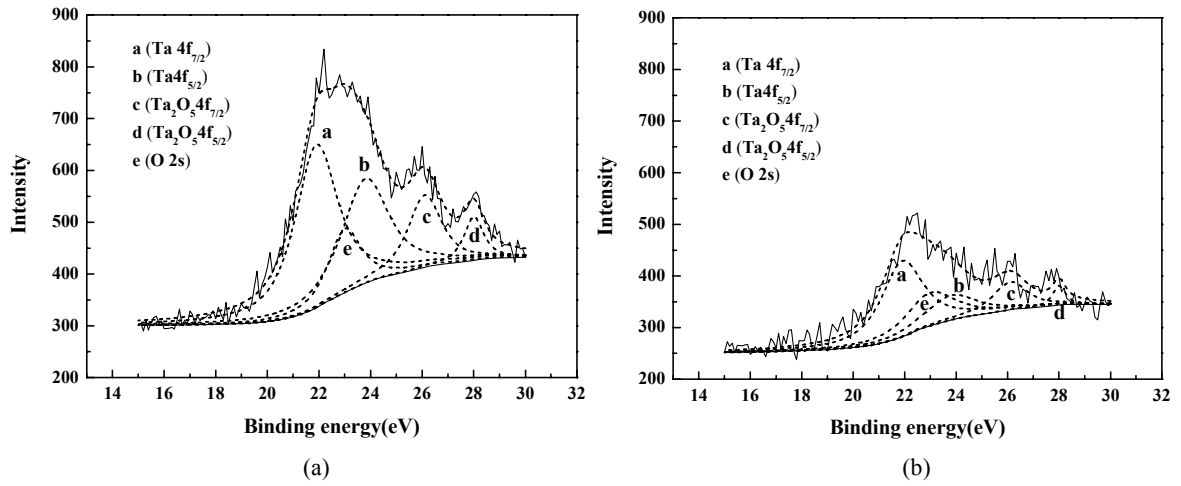


Fig. 6. XPS spectra of Ta for specimen C, (a) level 3 (b) level 5 (solid line : experiment, dash line : calculation)

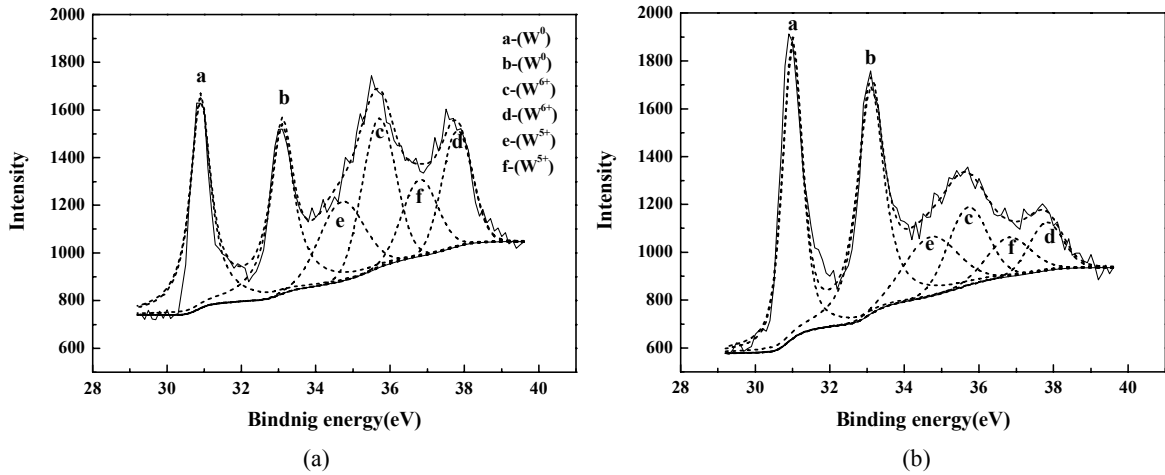


Fig. 7. XPS spectra of W for specimen B, (a) level 2 (b) level 3 (solid line : experiment, dash line : calculation)

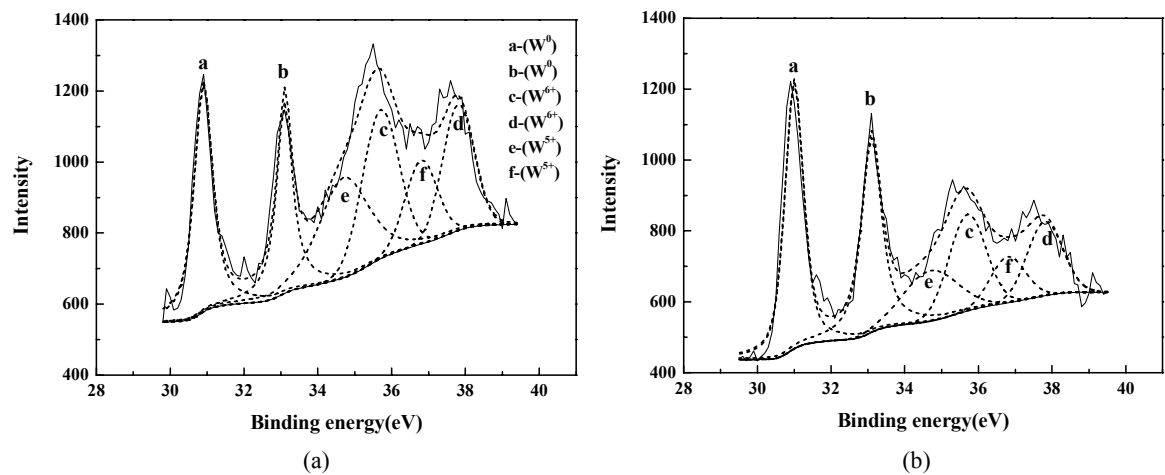


Fig. 8. XPS spectra of W for specimen C, (a) level 2 (b) level 3 (solid line : experiment, dash line : calculation)

C was indicated not only W^{6+} but also W^{5+} . This result is due to the formation of tungsten bronze by the double injection of an electron from an electrode and a charge compensating ion from the electrolyte into the interstitial sites of the tungsten oxide matrix.⁶⁾ Test solution is an acidic solution therefore hydrogen ion is inserted into the interstitial sites of W for charge compensation from the electrolyte. This leads to the formation of the tungsten bronze, H_xWO_3 . Injected electron in WO_3 is located at W atom creating a W^{5+} site. Electron can hop from a W^{5+} site to a neighboring W^{6+} site. However it is different to peak area of W^{5+} between specimen B and C. Peak area of W^{5+} in the specimens C is larger than specimen B. This means that formation of H_xWO_3 increases with addition of La and Ta. This result is considered as that added La forms La_xWO_3 and then formed La_xWO_3 increase H_xWO_3 formation in the passive film due to La^{3+}/H^+ ion exchange reactions.⁷⁾ So it seems that W^{5+} increases. In conclusion, addition of La and Ta in W-modified austenitic stainless steel shows not only better corrosion resistance but also better electrical property.

4. Summary

The electrochemical properties of W-modified austenitic stainless steels containing Ta and La were evaluated in

a H_3PO_4 type PEMFC environment. The results can be summarized as follows:

- (1) Electrochemical tests show Ta addition in W substitution stainless steel enhances corrosion resistance of austenite stainless steel by formation of Ta_2O_5 in PEMFC environment.
- (2) W substitution decreases contact resistance by formed H_xWO_3 in the passive film.
- (3) La addition in W-modified stainless steel increases electrical conductivity by formation of La_xWO_3 .

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