

Single Stack Performance using Chromium Carbide (Cr–C) and Niobium Carbide (Nb–C) Coated on 316 L Bipolar Plates

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ABSTRACT

Metallic bipolar plates tendency to have high contact resistance and corrosion after several times of usage affected performance of a cell in PEMFC stack. This study focused on the interfacial contact resistance (ICR) and corrosion resistance of SUS 316 L bipolar plates using Cr–C and Nb–C as coating layer, single stack performance in PEMFC were observed by experimental. The Cr–C and Nb–C coating layer acted as protective layer between SUS 316 L bipolar plates. Therefore, coating is a method in preventing the bipolar plates surface material from damage in the acidic environment of PEMFC. To develop corrosion-resistant and high conductivity bipolar plates for PEMFC, the coatings bipolar plates were applied to cell fabrication in comparison with bare SUS 316 L bipolar plates. The SUS 316 L bipolar plates size and electrode area were 50 mm² and 25 mm², respectively. The experiment was carried out on a prepared assembled single cell bipolar plates with the commercial membranes, conductive carbon papers and gasket. Initial performance of the single cells using Cr–C and Nb–C coatings over SUS 316 L bipolar plates were recorded at a cell voltage between 0.4 V to 0.5 V, respectively. In comparison, Nb–C gives good performance of corrosion resistance and the ICR value as low as 10⁻¹² A/cm² and 1.22 mΩ cm⁻². Additionally, it gives maximum power density of 137 mW/cm² at the cell voltage 0.51 V. The lifetime durability of the single cell significantly improved from the uncoated current density of 390 mA/cm² to 450 mA/cm² with Nb–C coating layer.

Keywords: Single stack performance; PEMFC; metal bipolar plates; Cr–C; Nb–C

INTRODUCTION

SUS 316 L bipolar plates in PEMFC are prone to corrodes at the cathode cell, hence decrease the electrical conductivity at the anode cell. Still, it is good in high electrical conductivity and mechanical strength, good machinability, and relatively low cost for mass production (Asri et al. 2017). Antunes et al. 2010 also recommended austenitic stainless steel types 316 and 316 L that uniformed good as metal bipolar plates. In addition, the chromium and nickel element in the austenitic stainless steel have good in corrosion resistance (Mele et al. 2012). These types of metal are superior with the high weight percentages of Cr and Ni, hence increase electrical conductivity as well in the PEMFC (Arwati et al. 2018).

Modification on the surface metal is needed to overcome this problem (Asri et al. 2017; Taherian 2014). Cr–C (chromium carbide) and Nb–C (niobium carbide) were suggested as coating on bipolar plates. Hence, transition metal carbides and nitrides possess prominent

physical and chemical properties such as superconductivity, high hardness, high melting point up to 2204 °C, chemical stabilization and high corrosion resistance (Ghahfarokhi et al. 2016; Caihong et al. 2016). Since the bipolar plate requires fabrication of channels in the plate surfaces, SUS 316 L have high ductility in order ease of manufacturing processes especially for mass production compared to graphite (Lyons et al. 2016).

Previous studied on mechanical performance of polymer carbon composite (CCP) recommended used for HT-PEMFC application, but the mixed composites also failed to sustain the durability at low temperature of fuel cell plate instead of low electrical conductivity (Husaini et al. 2018; Radzuan et al. 2017). As SUS 316 L was readily made materials, as well as not complex material preparation needed as ceramic polymers, high conductivity and corrosion resistance will attain the bipolar plates endure for long terms operation in PEMFC environment (Karimi et al. 2012). In the nut shell, hydrogen could be the key to powered vehicles or certain energy application without emitting harmful carbon dioxide,

and potentially replacement to fossil fuel as an energy storage medium (Hosseini et al. 2016).

MATERIALS AND METHODS

FABRICATION OF BIPOLAR PLATES AND METHOD DETAILS

SUS 316 L plates with thickness 3 mm were prepared to form flow channel for gas and cooling water, with serpentine flow field designed of 25 x 1 x 0.8 mm. The bipolar plates were ultrasonically cleaned in acetone for 30 minutes to remove any contaminants from the metal's surface before sputtering. For single cell test, two prepared plate for anode and cathode side with the flow channel were ready to sputtering with each set with Cr-C and Nb-C coating.

EQUIPMENTS AND TOOLS

The ICR was observed at the temperature of 40 °C, 60 °C, 80 °C and 100 °C. The applied current was at 1 A and 150 N cm⁻² compaction force. Current (I) was sent in a complete setup and potential (V) was measured through a circuit in different preheating temperatures of 40 °C, 60 °C, 80 °C and 100 °C. The ICR setup and measurement calculation of surface contact resistance testing was measured by Keithly Meter device (Aryani et al. 2016).

Electrochemical measurements were conducted on a Metrohm equipment by potentiodynamic polarization. A coupon shaped used as substrate at room temperature in a solution of 0.5 M sulphuric acid (H₂SO₄). The SUS 316 L substrate was used as the working electrode, a saturated calomel electrode Ag/AgCl (SCE) was used as reference electrode, and a platinum electrode acted as the counter electrode. The substrate was stabilized at open circuit (OCP) for 1 h and was polarized from OCP with a scan rate of 1 mV/s.

The surface of the plates coated with Cr or Nb (purity 99.99 wt%) and C (purity 99.99 wt%) were used as the target with supplied DC and RF power. The commercial target measuring was 3 and 101.6 mm in thickness and diameter by using PVD magnetron sputtering. The distance DC (Cr/Nb) and RF (C) to substrate holder were approximately 120 mm and 145 mm. The shutter was closed and pre-sputtering was conducted for 12 hour and evacuated to 4.6 x 10⁻⁶ Torr and purged with Ar gas (Asri et al. 2019). The sputtering process in the PVD chamber started after vacuum pumping to 2.0 x 10⁻² Torr. The magnetron sputtering system used argon as the working gas mixed with reactive gas of nitrogen to improve the structures and properties of sputtered coating (Asri et al. 2019; Alresheedi et al. 2017).

SINGLE CELL TEST

Five layered membrane electrode assembly (MEA) with active area 25 x 25 mm, integrated gas diffusion layers (GDL) were used. Pt loading was 0.5 mg/cm² and a membrane Nafion® 212 type with 0.002" thickness, attached with 410

um thick carbon cloths GDL. Single cells were assembled with the MEA, carbon papers, gasket and the prepared bipolar. The carbon paper used as the conductive electron might not be disturb by the gap to be filled between the gasket and the MEA, since the commercial MEA used did not support to balance the thickness gap between the gasket and the membrane during stacking. The single cell PEMFC operates with providing humidified hydrogen and oxygen gases through the anode and cathode, respectively. I-V curves were measured using flow meter indicator attached to the voltmeter for evaluated the performance of single cells.

RESULTS AND DISCUSSION

MATERIAL CHARACTERIZATION USING ENERGY DISPERSIVE X-RAY

Table 1 show nominal compositions of SUS 316 L plates before and after coating with Cr-C and Nb-C. The element weight percentages were gained from the EDX analysis. The samples of disk shaped (coupon) with a thickness of 3 mm were recommended to provide lightweight material to sustain with reasonable strength for the bipolar plates (Kahrahman et al. 2017). The nominal composition showed that the main major component in SUS 316 L plates consists of Cr and Ni with 16 wt% and 10 wt%, respectively. By coating SUS316 L with corrosion-protective of Cr-C and Nb-C layer, only the nominal composition of carbon (C), chromium (Cr) and niobium (Nb) were analyzed to investigate the relationship between interfacial contact resistance (ICR) and corrosion behavior as preparation for single cell performance lifetime with the coatings. Figure 1 shows the EDX results aimed for C, Cr and Nb elements that gives major concerned for changes after coatings. Cr-C coated consists of C and Cr with 43.27 wt% and 56.73 wt%, respectively. Meanwhile, Nb-C coated consists of C and Nb with 73.05 wt% and 26.95 wt%. In comparison, coating of Cr-C has low C content than Nb-C. To assure the electrical properties and corrosion resistance affected by these two elements, AFM and hardness test were measured.

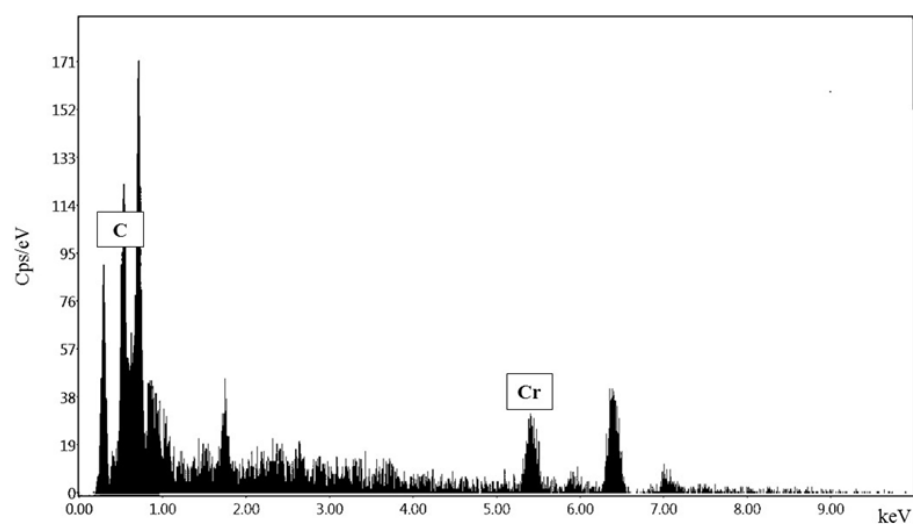
SURFACE ROUGHNESS AFTER COATING

The surface roughness and the step height of SUS 316 L at different parameters for Cr-C and Nb-C were examined using AFM, and the results are shown in Table 2. The AFM images show the detailed surface feature of the half-covered Cr-C and Nb-C coatings on the SUS 316L plates. Due to step height thickness preparation, the ridges created on the surface plates by polishing instead of half covered with the masking tape. A 3D roughness image shows a growth of granular shaped grain on the coated surfaces. The roughness value for Cr-C and Nb-C were 222.26 nm and 202.79 nm, respectively.

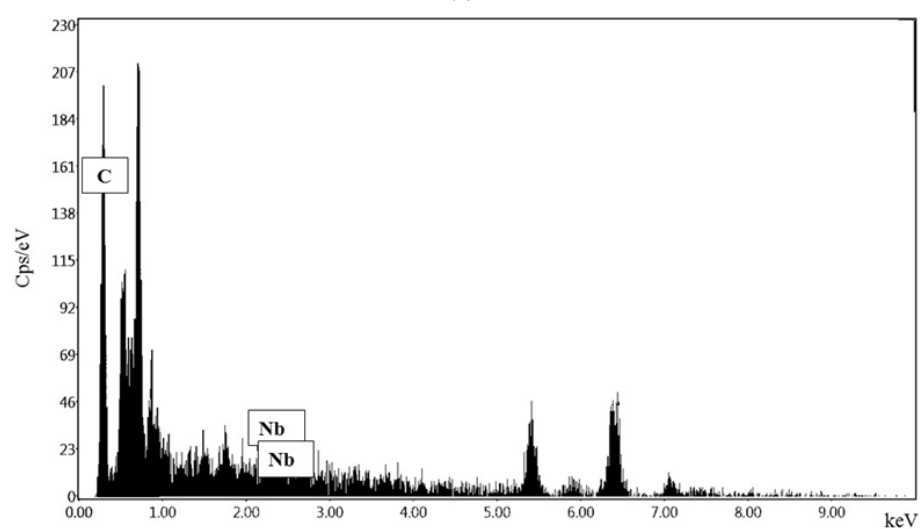
In addition, both roughness value of coated depends on the DC power and deposition time of sputtered. Based on the coating parameter the, the ridges decreased with the increase

TABLE 1. Nominal composition of SUS 316 L with coating of Cr-C and Nb-C.

Types of material	SUS 316 L	Cr-C coated	Nb-C coated
Element	wt %	wt %	wt %
Carbon (C)	<0.03	43.27	73.05
Manganese (Mn)	1.00	—	—
Phosphorus (P)	<0.045	—	—
Sulfur (S)	<0.03	—	—
Silicon (Si)	<0.75	—	—
Chromium (Cr)	16.00	56.73	—
Nickel (Ni)	10.00	—	—
Molybdenum (Mo)	2.00	—	—
Nitrogen (N)	<0.10	—	—
Iron (Fe)	Balance	—	—
Niobium (Nb)	—	—	26.95



(a)



(b)

FIGURE 1. EDX analysis after coatings (a) Cr-C coating layer and (b) Nb-C coating layer.

of DC power and deposition time (Asri et al. 2019). It clearly observed that lesser ridges and thicker layer observed for Nb-C coated with gas flow rate of 8 sccm, 100 W supplied and 80 minutes of deposition than Cr-C coated (8 sccm, 80 W and 60 min). These parameters were the best results that was experimented using Taguchi as a tools. In addition, microhardness test were intended at 5 regions of Cr-C and Nb-C coated. The hardness increased after coatings as show in the different regions of the surface before and after coating surface of SUS 316 L. From profile pattern, the average values were 205 and 211 HV, and increased after Cr-C (228 HV) and Nb-C (220 HV) coated. The influenced of hardness have correlation with the elements content as stated in measured.

ELECTRICAL PROPERTIES

The ICR was measured at temperatures of 40 °C, 60 °C, 80 °C and 100 °C. As shown in Table 3, the ICR trend with the current of 1 A for each sample was observed. The SUS 316 L plates without coating were obtained at high temperature with low ICR values. From the measured data, the ICR values decreased as the temperature increased, as well as the SUS 316 L have been coated.

The graph pattern in Figure 2 indicates the ICR values of SUS 316 L plates versus temperature. Overall, the ICR values decreased with the increase of temperature from 40 °C to 100 °C. Nb-C coated had a lower ICR values compared with other samples, and also presented the same general behaviour. Although, the ICR values for SUS 316 L was higher before coating, thus it still below than 10 mΩ cm² for U.S DOE requirement. The ICR values increased by the order of Nb-C coated > Cr-C coated > bare 316L. Hence, Nb-C coated remained an excellent candidate as metal bipolar plate for PEMFCs since the small differences in ICR values. Although Nb-C formed in a small ranged as in Figure 1 (b), it gives greater availability for Nb-C good in corrosion resistance and sustain the ICR for better electrical conductivity in compared with Cr-C. The niobium element is in group 5 in periodic table was superconductive and high corrosion resistance, hence the physical characteristic super improved when combined into carbides element.

The difference percentages of the ICR values before and after coating with Cr-C and Nb-C at 40 °C and 100 °C were 62 % and 73 %, respectively. Accordingly, SUS 316 L observed to be improved less than 40 % the ICR values from its initial value after coating, as specified in Table 3. The influence of low temperature on austenitic stainless

TABLE 2. AFM images of step height profiles and roughness that were half covered to enable thickness after coating.

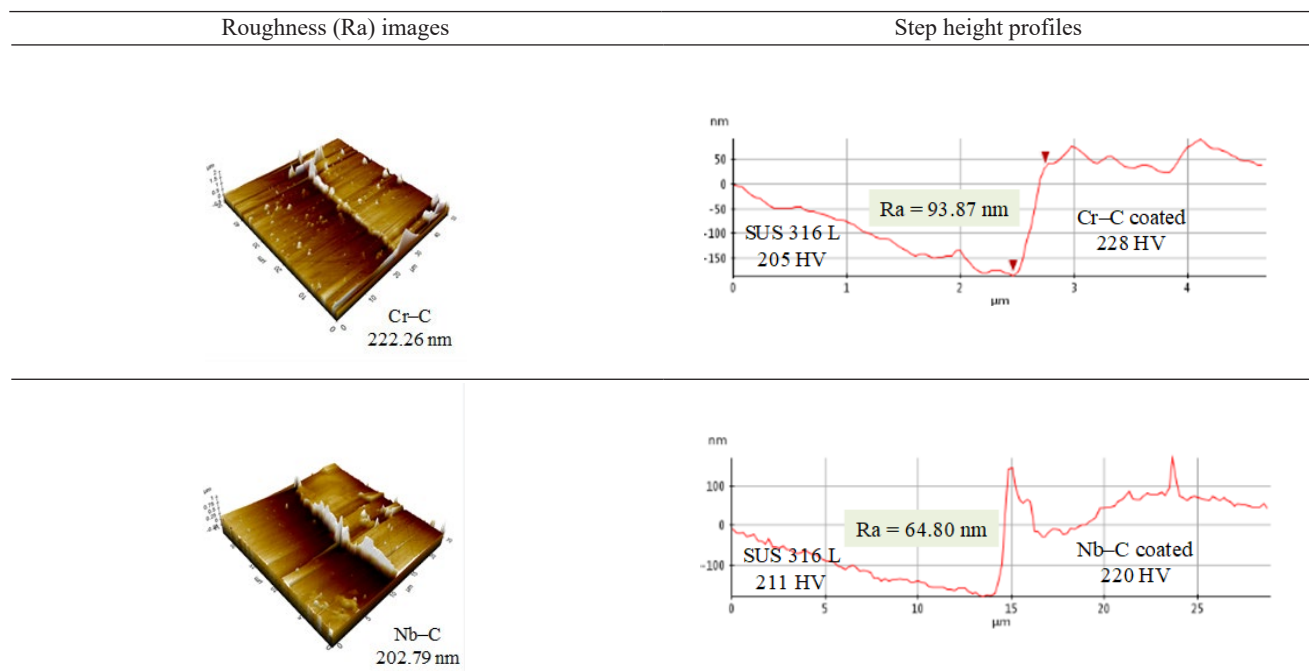


TABLE 3. The ICR and potential (V) for SUS 316L with different coating parameter at 1 A.

Material	SUS 316 L		Nb-C coated		Cr-C coated	
	V (V)	ICR (mΩ cm ²)	V (V)	ICR (mΩ cm ²)	V (V)	ICR (mΩ cm ²)
T (°C)						
40	2.94	4.63	1.40	2.43	1.67	3.01
60	2.29	3.60	1.29	1.58	1.59	2.18
80	1.89	2.97	1.10	1.25	1.57	1.72
100	1.67	2.63	0.89	1.22	1.45	1.55

steels that contained high Cr and Ni (as in Table 1) relatively reduced the ICR with the increase of temperature, as in Figure 2. Overall, Nb-C coated obtained the lowest ICR values after coating. The ICR values for SUS 316 L plates after Nb-C and Cr-C coated at 100 °C were 1.22 mΩ cm² to 1.55 mΩ cm², thereby meeting the requirement of U.S DOE.

Potentiodynamic polarization tests were conducted to evaluate the corrosion behavior of uncoated SUS 316 L, Cr-C and Nb-C coated samples. Figure 3 shows the polarization curves of the samples. It can be observed the graph pattern in the trans-passive potential region of

the anodic polarization curves. Cr-C and Nb-C coated efficiently protected the SUS 316 L substrates based on the polarization test results.

Table 4 shows the reading measurement gained from Tafel polarization curves using Methrohm software. The corrosion rate occurred based on the corrosion current density (I_{corr}) and potential (E_{corr}) for each sample. The OCP values for SUS 316 L, Cr-C and Nb-C coated were -0.7, 0.006 and -0.07 V (Ag/AgCl) in H₂SO₄ solution. Overall, the highest E_{corr} was produced by Cr-C coated. The sample was in passive state under test condition starts from -0.35,

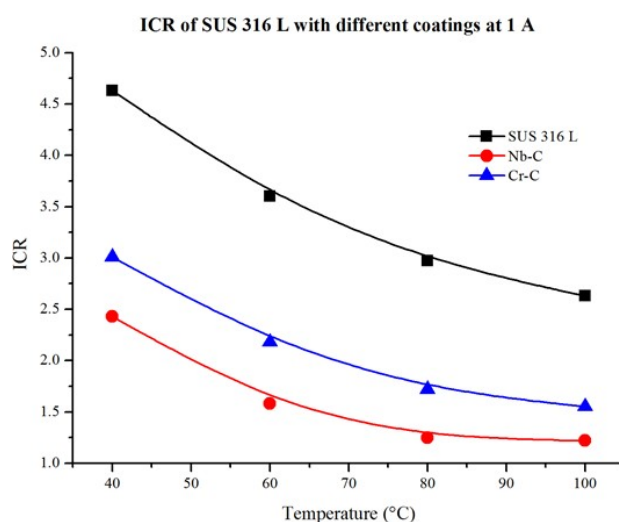


FIGURE 2. The ICR pattern for SUS 316 L with different coating parameters at 1 A over temperature

TABLE 4. Electrochemical parameter properties of SUS 316 L with Cr-C and Nb-C coating.

Sample	E_{corr} (mV)	I_{corr} (A/cm ²)	CR (μm/year)
SUS 316 L	-709.47	1.75×10^{-9}	2.03
Cr-C coated	6.98	3.93×10^{-9}	0.45
Nb-C coated	-78.36	137.71×10^{-12}	0.18

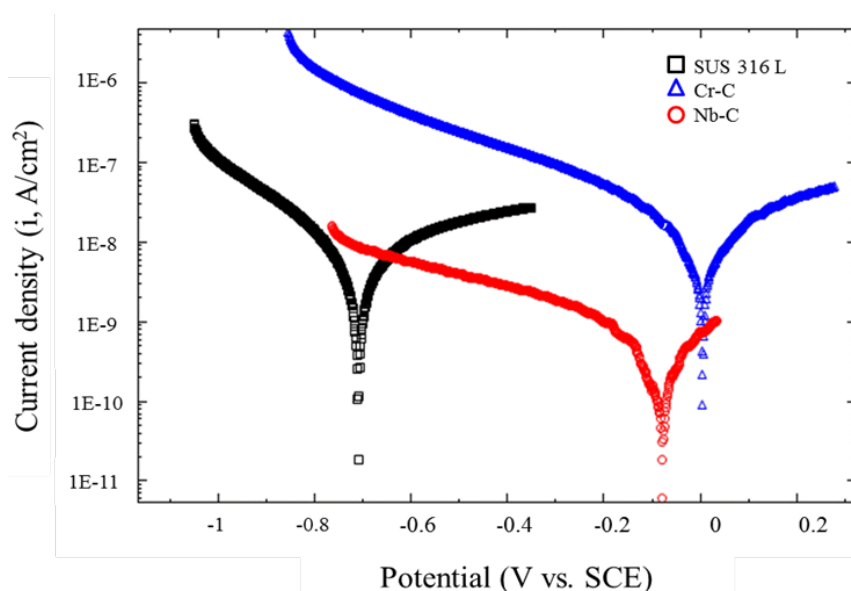


FIGURE 3. Polarization curves for SUS 316 L with Cr-C and Nb-C coatings in 0.5 M H₂SO₄

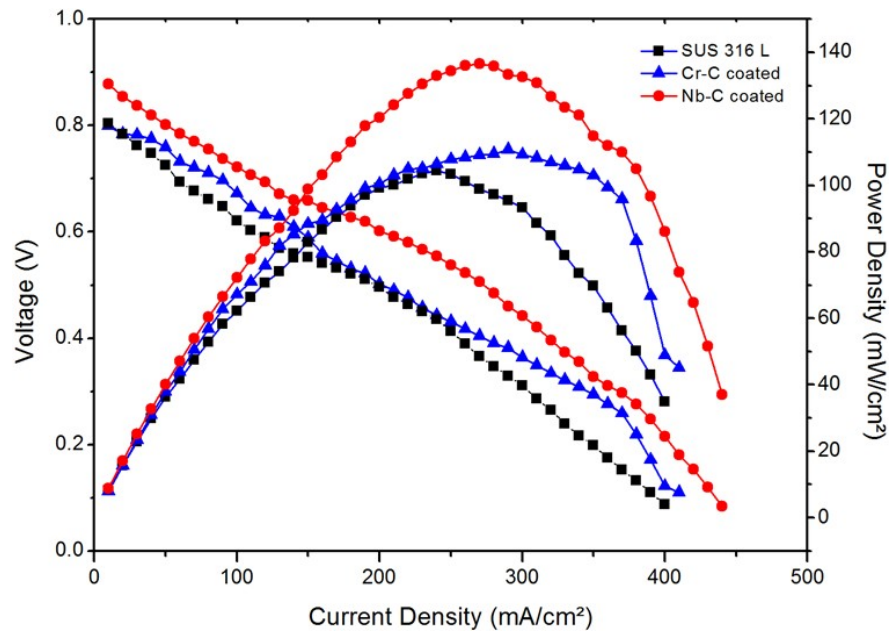


FIGURE 4. i - V curves for the single cell stack; active electrode area = 5 cm², $T_{\text{cell}} = \text{RT}$, $\lambda_{\text{H}_2} = 0.5$, $\lambda_{\text{O}_2} = 5$, and $P = 1$ atm

0.28 V and 0.6 V, for SUS 316 L, Cr-C and Nb-C coated at room temperature with similar general features, respectively. Corrosion occurred due to the increase of current densities. A passive layer formed on the surface in an acidic solution that provides an aggressive medium for the samples, based on the measurement reading.

As theoretical principle calculation for corrosion rate of electrochemical measurement is based on ASTM G102-89. Hence, experimental using software, the I_{corr} and E_{corr} were calculated from the intercept of the Tafel slopes to get the corrosion rate. Cr-C coated exhibited much better corrosion resistance than SUS 316 L and the I_{corr} recorded was 3.93×10^{-9} A/cm², respectively. However, the lowest I_{corr} 137.71×10^{-12} A/cm² was recorded by Nb-C coated. The delay of corrosion processed from the passive region decreased the corrosion rate before trans-passive behavior to the anodic region. Therefore, decreasing of I_{corr} in the anodic branch using PVD coatings was slower for the coated sample than uncoated SUS 316 L, with lowest I_{corr} which satisfies U.S DOE.

SINGLE CELL PERFORMANCE

The surface roughness and the step height of SUS single cells were tested using uncoated SUS 316 L, Cr-C and Nb-C coated to evaluate performance of the bipolar plates. The measured reading taken after 2 h operated for activation. The activation released the hydrogen and oxygen gases flows to the anode and cathode cell stabilized with the voltage consistently increased in the system. The initial performance of the single cell were shown in Figure 4. From the i - V curves, the performance of SUS 316 L increased after Cr-C and Nb-C coated. At the cell voltage of 0.43 V, the single

cells employed by SUS 316 L bipolar plates was 104 mW/cm². After coating with Cr-C and Nb-C, at the cell voltage 0.38 V and 0.51 V, the cells produced 111 mW/cm² and 137 mW/cm², for the maximum power density.

In this study, the current density before coating was lower for the single cell bipolar plates. Due to the lifetime after coating was prolonged more than 400 mA/cm², and the performance reduced slowly and steadily operates, Cr-C and Nb-C coated improves the cell performance. However, the challenges are to sustain and maintain the initial performance with good operating condition above 0.6 V as a function of operating time (Shimpalee et al. 2016). To summarize, the performance pattern for Cr-C and Nb-C coated increased 6 % and 24 % after coating.

CONCLUSION

SUS 316L samples were sputtered and formed Cr-C and Nb-C coated to determine the improvement in corrosion current density and ICR. The potentiostatic tests showed the good performance of corrosion resistance as low as 10^{-12} A/cm² for Nb-C, and the ICR achieved at $1.22 \text{ m}\Omega \text{ cm}^{-2}$ with increasing temperature. It also gives maximum power density of 137 mW/cm² at the cell voltage 0.51 V. Cr-C and Nb-C elements after coating aided in improving the mechanical properties and corrosion resistance of SUS 316 L to serve as bipolar plates. The single cell successfully improved the current density of the uncoated bipolar plates from 390 mA/cm² to 420 mA/cm² and 450 mA/cm² after coating. An improvement on the SUS 316 L bipolar plates were successfully developed Cr-C and Nb-C layer to sustain the performance of single cell due to high corrosion resistance at anode cell and as well as increase the electrical conductivity at cathode cell.

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DECLARATION OF COMPETING INTEREST

None.

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