



Short communication

Direct observation of the passive layer on high nitrogen stainless steel used as bipolar plates for proton exchange membrane fuel cells

Masanobu Kumagai^{a,b,1}, Seung-Taek Myung^{c,*}, Hitoshi Yashiro^d, Yasuyuki Katada^{e,**}^a Materials Creation and Reliability, National Institute for Material Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan^b Taiyo Stainless Spring Co., Ltd., 2-8-6 Shakujicho, Nerimaku, Tokyo 177-0041, Japan^c Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul 143-747, South Korea^d Department of Chemistry and Bioengineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan^e Collaboration Planning, National Institute for Material Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

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ABSTRACT

The purpose of this report is to directly observe the passive layer and concentration behavior of nitrogen interstitially incorporated in Ni-saving high nitrogen stainless steel (HNS) using an aberration corrected scanning transmission electron microscopy–energy dispersive spectroscopy (STEM-EDS) or – electron energy loss spectroscopy (EELS). The thickness of the passive layer barely changed after 1000 h single cell operation, compared with the as-polished state. The observed passive layer was thin (3 nm) and mainly composed of chromium oxide, as confirmed by STEM-EDS. It was confirmed that nitrogen was not present in the passive layer, but was concentrated at the interface between the passive layer and the metal bulk. The concentrated area ranged approximately 2 nm to steel bulk from the interface. With help of the STEM-EDS and EELS, we were able to understand the nature of the passive layer for Ni-saving HNS, which caused remarkable improvement of the cell performance due to superior corrosion resistance.

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1. Introduction

Recently, the fluctuation of nickel prices has given rise to the possibility of replacing the expensive nickel to other inexpensive elements in austenitic stainless steel. And yet, the resulting corrosion resistance is expected to be equivalent to the Ni-containing stainless steel. Nitrogen is cheap and plentiful in the earth, and so the application of the element for the improvement of steel properties is quite attractive. For this reason, we have developed Ni-saving HNS to decrease the concentration of nickel down below 4 mass% through the interstitial incorporation of nitrogen by the pressurized electro-slag remelting (P-ESR) method in NIMS, maintaining the original austenitic phase and other physical properties as well [1]. As a result, strength and corrosion resistance of Ni-saving HNS were greatly improved by enlarging the solubility range of nitrogen [1–11].

A great deal of effort has been made to understand how the nitrogen element in steel behaves to show superior corrosion resistance. Several spectroscopic investigations were conducted

to analyze the behavior of the nitrogen in steel by AES [4,12], SIMS [13], and XPS [8,12,14]. For type 304LN stainless steel, the chromium oxide ratio in the passive films was higher than that of the type 304 one in chloride environment, as confirmed by SIMS [13]. For the polarized Ni-saving HNS in artificial sea water, the nitrogen in the steel was concentrated to the interface of passive layer and matrix, as confirmed by XPS [8].

As Ni-saving HNS exhibits superior corrosion resistance, we have employed the steel as bipolar plates for PEMFCs. According to our prior results [10,15], Ni-saving HNS employing cell demonstrated excellent cell performance, which is compatible to that of the graphite bipolar plate employing cell. Also, we have speculated the possible reason for the good cell performance by means of XPS analyzing the passive layer after the cell operation. However, we do not yet fully understand the role of nitrogen and passivation in the fuel cell environment. In this report, we, for the first time, confirm the distribution of N element existing in the passive layer that affects superior cell performance of Ni-saving HNS in PEMFC operation conditions.

2. Experimental

A single cell was assembled that adopted Ni-saving HNS and a commercially available MEA (carbon cloth type gas diffusion layers) with a compressive force of 150 N cm⁻² controlled by a torque wrench. The active electrode area was 50 mm × 50 mm. The single

* Corresponding author. Tel.: +82 2 3408 3454; fax: +82 2 3408 3454.

** Corresponding author. Tel.: +81 29 859 2112; fax: +81 29 859 2886.

E-mail addresses: smyung@sejong.ac.kr (S.-T. Myung),KATADA.Yasuyuki@nims.go.jp (Y. Katada).¹ These authors equally contributed to this work.

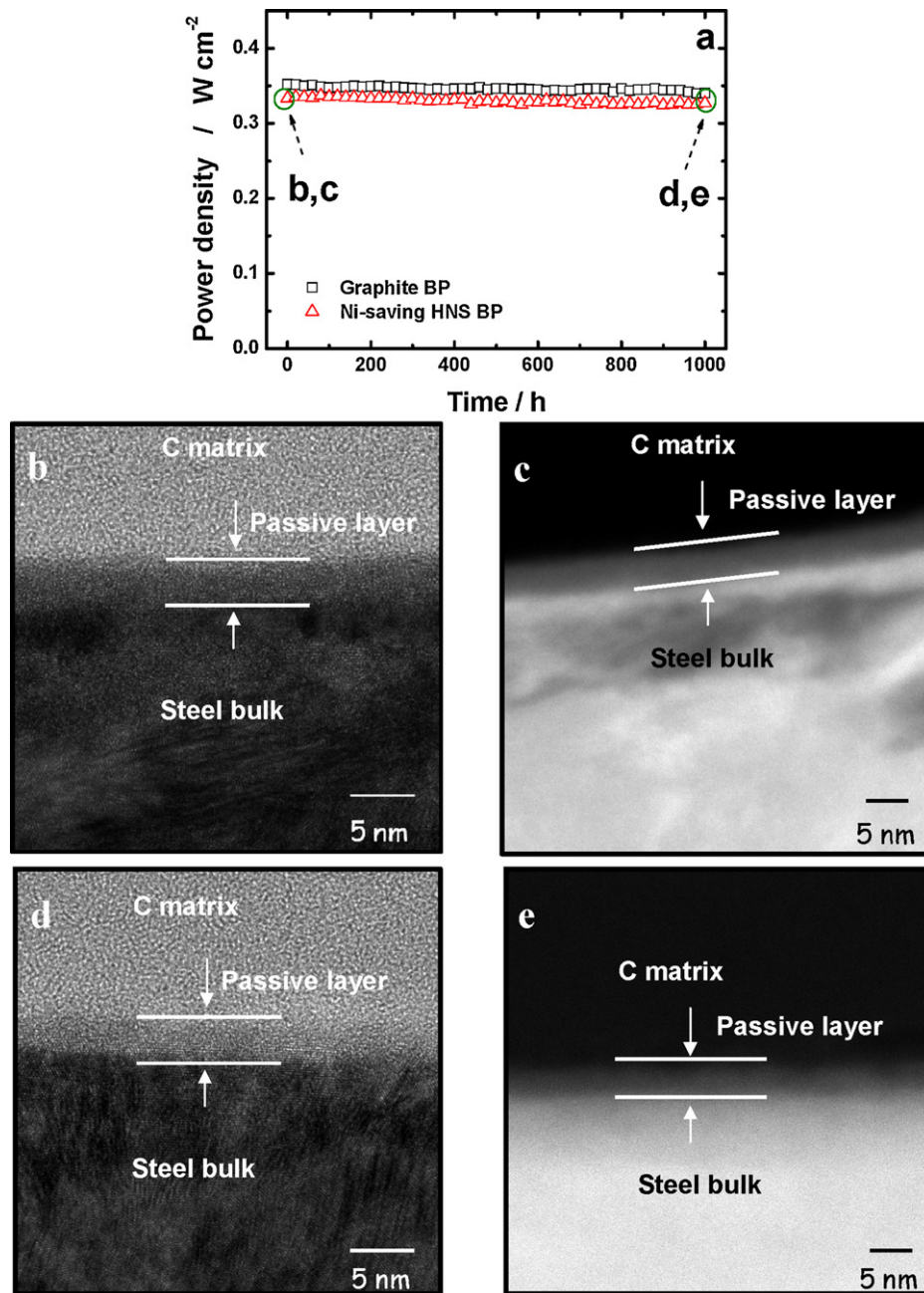


Fig. 1. Power density variation during 1000 h cell operation using different bipolar plate (a) TEM bright-field images (b: as-polished state, d: cathodic side after 1000 h cell operation) and HAADF-STEM images (c: as-polished state, e: cathodic side after 1000 h cell operation) of Ni-saving HNS.

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 (H₂) and 40% for air with flow rates of 0.124 NLPM and 0.520 NLPM, respectively. The applied current density was 0.5 A cm⁻² (12.5 A).

After the cell operation for 1000 h, the cell was disassembled and the bipolar plate in cathode side was cut to an appropriate size for TEM observation. The sample was prepared using a focused ion beam (FIB) and loaded on a copper mesh, and then it was processed as thin as possible by Ga⁺ ion beam at an acceleration voltage of 30 kV. The sample was observed by aberration corrected STEM (FEI Titan80-300) with EDS (AMETEK *r*-TEM) and EELS (Gatan GIF Tridiem model 863) at an acceleration voltage of 200 kV. For the analysis of nitrogen, due to the lower X-ray scattering factor of nitrogen, line profile analysis by EELS was carried out parallel to

passive film. Nitrogen was analyzed by 1 nm from the inner passive layer to the matrix. Using 0.2 nm of beams, the sample was analyzed at 20 nm.

3. Results and discussion

Fig. 1a shows the power variation at the time of the single cell adopting Ni-saving HNS bipolar plates in its naked state. It is obvious that there is no significant change in power, compared with the cell using graphite bipolar plates. Therefore, we believe that Ni-saving HNS is able to replace present graphite bipolar plates. In other words, Ni-saving HNS provides the best level of corrosion resistance ever been achieved in the metallic bipolar plate system in the PEMFC operation environment. The reason for the excellent

Table 1
Chemical composition of the Ni-saving HNS (mass%).

	C	S	Mn	Cr	Ni	Mo	N	Fe
Ni-saving HNS	0.022	0.0005	3.09	24.07	3.88	1.94	1.06	Bal.

performance of Ni-saving HNS bipolar plates would be essentially associated with good stability of passive layers. Therefore, the passive layer needs examined to confirm whether it remains intact or not when the cell performance is good, as shown in Fig. 1a. Since strong energy sources such as XPS, AES, and SIMS may cause serious deformation of the passive layer, we have chosen the direct observation of the passive layer by TEM. The as-polished exhibited a thin layer ranged 3–4 nm thickness for the bright-field TEM image (Fig. 1b) and high angle annular dark field (HAADF)-STEM image (Fig. 1c). For the TEM images, the sample is rib surface of center part. Interestingly, there is no noticeable change in the thickness or integrity of the passive layer for the used bipolar plate (Fig. 1d and e), compared with the as-polished. Usually, passive layers on austenitic stainless steel are as thin as several nm [16] but the layers are inclined to be swollen to even thicker than 10 nm during cell operation to increase unfavorable contact resistance. According to our prior report [15], the corrosion trace such as pitting/crevice corrosion was not observed with the surface or depth direction. The thickness of the passive layer on Ni-saving HNS bipolar plate after 1000 h cell operation was estimated to be 3–4 nm by XPS [10], which is in accordance with the present TEM results (Table 1).

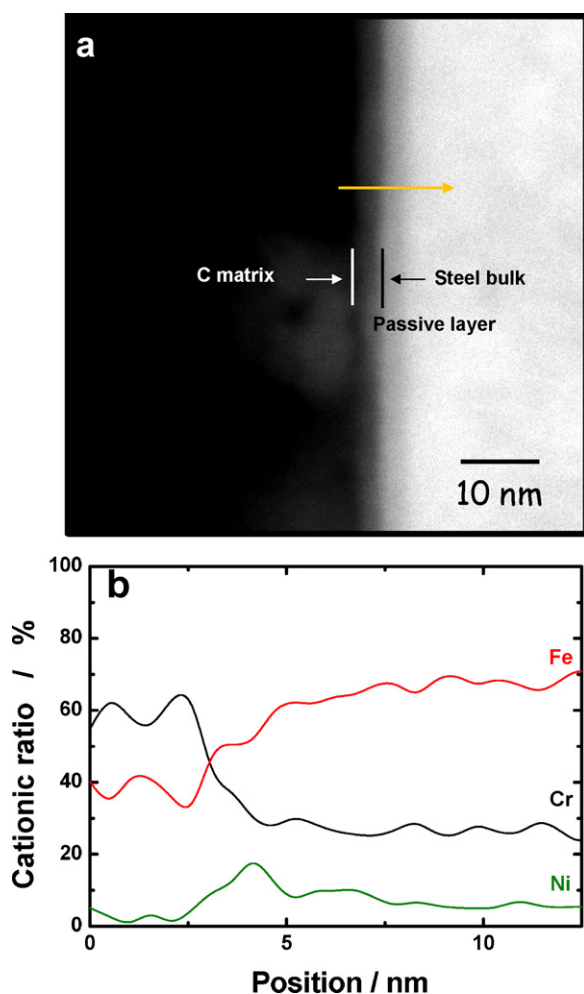


Fig. 2. HAADF-STEM image (a) and EDS line profile (b) of Ni-saving HNS bipolar plate for the cathodic side after 1000 h cell operation.

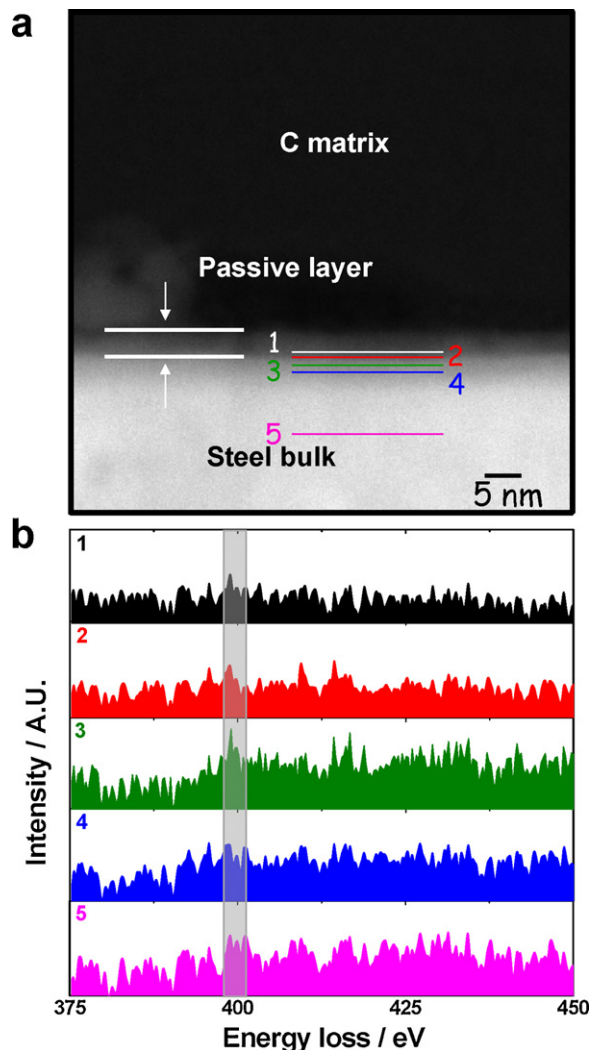


Fig. 3. HAADF-STEM image (a) and EEL line profile (b) of Ni-saving HNS bipolar plate for the cathodic side after 1000 h cell operation.

As we already recognize, the thinner thickness is related with the composition of the passive layer. Fig. 2 shows the result of the HAADF-STEM image (Fig. 2a) and the EDS line profile (Fig. 2b) of the cathode side after 1000 h cell operation. The measured samples were iron, chromium, and nickel. The relative intensity of the chromium increased, compared with that of iron in the passive layer. Similar tendencies were reported with that of our prior XPS studies [10,17–19]. Besides, nickel was not identifiable in the passive layer. It is suggested that nickel is concentrated at the interface between the passive layer and steel bulk. The sensitivity of nitrogen is lower than that of other metallic elements, so we applied the EELS line analysis (Fig. 3). A line scan was performed at 5 places, that is, from passive layer to steel bulk. A nitrogen-related peak is observed at round 400 eV for Ni-saving HNS [20]. According to prior literatures [21], it has been known that nitrogen is concentrated at the interface between the passive layer and steel bulk. Similarly, the nitrogen-related peak was hard to be found in the passive layer, even at the interface (Fig. 3b-1 and -2). Surprisingly, the soluted nitrogen-related peak was observed beneath the interface, which is located just 1 nm away from the interface (Fig. 3b-3). The existence form of nitrogen is soluted nitrogen or probably chromium nitride in Ni-saving HNS [21]. Nitrogen is known to dissolve as NH_4^+ ions [22–24] or NO_3^- ions [3,7,25,26]. The passive layer on Ni-saving HNS bipolar plate is mainly composed of chromium oxide

after 1000 h cell operation. Thus, it is considered that the nitrogen or chromium nitride in Ni-saving HNS is oxidized to NO_3^- ions with the simultaneous generation of H^+ ions in the PEMFC cathodic environment. From the TEM observation, it is clear that the passive layer of Ni-saving HNS is composed of an oxide component, mainly chromium oxide, and there is no nitrogen element in the passive layer. Furthermore, the soluted-nitrogen element was found in the steel bulk and was concentrated at 1 nm away from the interface. Therefore, the steel bulk is the reservoir of nitrogen to reduce the local pH of the passive layer by forming NO_3^- ions, due to the simultaneous generation of H^+ ions. A series of this process induces the chromium oxide based passive layer, and the passive layer provides significant corrosion resistance though the thickness of the film is thin as slim as 3–4 nm even after the fuel cell operation.

4. Conclusion

The role of nitrogen in Ni-saving HNS was traditionally investigated by AES, SIMS, XPS, and mean information about the depth direction was provided to these methods. In order to clarify the position of nitrogen enrichment, we adopted an aberration corrected STEM-EELS. Simultaneously, in order to demonstrate the properties of the passive layer on Ni-saving HNS, we applied an aberration corrected STEM-EDS. According to STEM-EDS, it is obvious that the chromium oxide-based passive layer of 3–4 nm thick was kept on the surface of Ni-saving HNS after 1000 h cell operation. It is clear that the soluted-nitrogen in HNS is concentrated to the matrix side of the interface between the passive layer and the matrix, and the concentration position is a range from approximately 1–2 nm from the interface. By the combination of STEM-EDS and EELS measurements, the characteristics of the passive layer and the concentration behavior of nitrogen are evident.

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