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Degradation behavior of a polymer electrolyte membrane fuel cell employing metallic bipolar plates under reverse current condition

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ABSTRACT

To examine durability of metallic bipolar plates (BPs) under reverse current conditions, the degradation of PEMFC employing graphite, bare 316L, and CrN-coated 316L BPs is investigated via a 1.4 V pulse cycling test. After 20 cycles, the average voltage decay rate at 160 mA cm^{-2} is 6.8, 16.8, and 12.0 mV $cycle^{-1}$ for the single cell using graphite, bare 316L, and CrN-coated 316L BPs, respectively. SEM, EPMA, and TEM analyses of the cathodes that experienced an extraordinary high voltage of 1.4 V show that carbon corrosion and Pt migration/agglomeration occur similarly for the single cells, irrespective of the bipolar plate material. In contrast, in the membrane tested with bare 316L and CrN-coated 316L, Fe and Cr are detected; the amounts of Fe and Cr in the membrane are higher for bare 316L than for CrN-coated 316L. The membrane contamination results in a decrease in the ionic conductivity of the membranes, which mainly contributes to the faster performance decay of the single cells employing bare 316L and CrN-coated 316L bipolar plates. Thus, if automotive PEMFCs using metallic BPs are exposed to reverse current conditions upon start/stop cycles, metal contamination of the membrane could accelerate the performance decay in addition to the cathode degradation, such as carbon corrosion and Pt migration/agglomeration.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are composed of membrane electrode assembles (MEAs), bipolar plates (BPs), and gas diffusion layers (GDLs). The BPs control the gas distribution, electrical connection, and water and heat management as well as contribute greater than 80% of the stack volume and weight [1]. Thus, they are required to have high electrical conductivity, good mechanical strength, formability, and corrosion resistance to the strongly acidic environment of the Nafion membrane. Most of the previous PEMFC stacks used graphite BPs [2–4]. However, due to the high cost, metallic BPs that are mostly fabricated from stainless steels have replaced graphite BPs for fuel cell vehicles [2–8]. When applying stainless steels to the BPs for PEMFCs, the first problem is corrosion because stainless steels fulfill all the requirements mentioned above except corrosion resistance [2–8]. During the last decade, various commercial stainless steels such as AISI 316, 316L, 310, 304, 321, 347 and 904L have been employed as bipolar plate materials for PEMFCs but unfortunately have not proved to be sufficiently corrosion-resistant [2–4]; the long-term performance of the cells decayed as a result of corrosion of the stainless steel BPs, which led to the reduction in the electrical conductivity due to the formation of a surface oxide and poisoning of the MEAs by metal dissolution [2–4].

To solve these problems, materials such as metal nitrides (TiN [9,10], CrN [11,12], VN, and so on) with high electrical conductivity and corrosion resistance have been coated on the surface of stainless steels by physical vapor deposition (PVD), chemical vapor deposition (CVD), plasma coating, electroplating, etc. Some of the coating materials tested have been reported to be applicable to PEMFCs due to their excellent corrosion resistance and electrical conductivity [9–12] under static operating conditions (constant load or constant voltage) for stationary applications.

Under automotive operating conditions including start/stop cycles, the so-called reverse current condition occurs, where the cathode is locally exposed to a high voltage of approximately 1.4 V [13,14]. Previous studies showed that the high voltage present at the cathode accelerated MEA degradation due to severe carbon corrosion and Pt oxidation [13–18], as described in Eqs. (1) and (2). Thus, metallic BPs might corrode under the reverse current condition even though they exhibit long-term stability under the static operation conditions, i.e., at cell voltages lower than the OCV. For

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example, iron and chromium, major elements of stainless steels, can be corroded, as described by Eqs. (3) and (4) [19].

$$CO_2 + 4H^+ + 4e^- = C + 2H_2O, \quad E_r^o = 0.207\,V_{RHE}\ [16] \tag{1}$$

$$Pt^{2+} + 2e^- = Pt, \quad E_r^o = 1.12\,V_{RHE}\ [19] \tag{2}$$

$$Fe^{2+} + 2e^- = Fe, \quad E_r^o = -0.44\,V_{RHE}\ [19] \tag{3}$$

$$Cr^{2+} + 2e^- = Cr, \quad E_r^o = -0.74\,V_{RHE}\ [19] \tag{4}$$

Although the corrosion behavior of stainless steel-based BPs can be different at potentials higher than the OCV at normal operating voltages of approximately 0.7 V, the durability of such BPs have been tested only under normal conditions. In this study, to investigate the feasibility of metallic BPs for automotive PEMFCs that are frequently exposed to the reverse current condition, the degradation of single cells employing graphite, AISI 316L, and metal nitride coated 316L was examined under a 1.4 V pulse cycling test.

2. Experimental

2.1. Electrode preparation and cell operating conditions

Single cells were assembled with a commercial MEA (Gore 5710 series (an/ca) 0.4/0.4 mg Pt loading/C) with an active area of 25 cm^2, commercial GDLs (SGL 10BC, 415 μm thickness), and BPs composed of graphite, AISI 316L stainless steel, or chromium nitride coated 316L (CrN-coated 316L). The CrN was coated on the inside of BPs (gas channel part) entirely by a sputtering method. The CrN-coated 316L stainless steel exhibited excellent durability during the constant load test. The assembled single cells were activated at 0.4 V for 24 h at a cell temperature of 65 °C, using hydrogen and air with a RH of 100% without applied pressures of gases. After the activation, the single cell was operated at a cell temperature of 65 °C with a stoichiometric ratio (SR) of 1.5 fuel (H_2) and 2.0 oxidant (air).

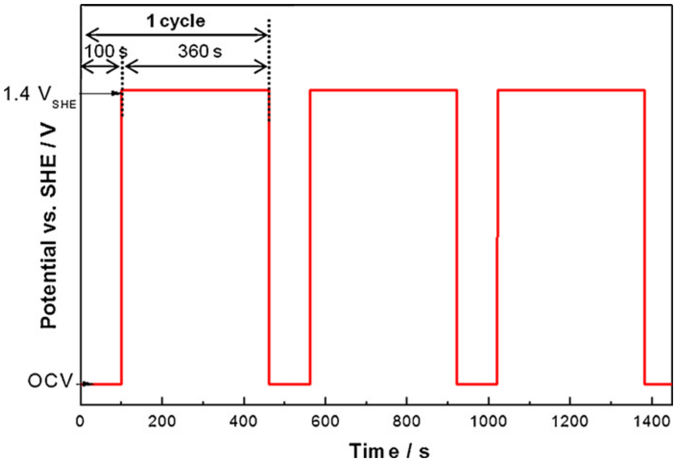

Fig. 1. Illustration of the 1.4 V pulse cycle employed in this study to accelerate the degradation of the cell performance under the reverse current condition upon start/stop cycles [15].

2.2. Accelerated durability test using 1.4 V pulse cycling

As an accelerated stress test (AST), 1.4 V pulse cycle tests were performed as described in Fig. 1 [15]. The prepared single cells were at open circuit voltage (OCV) for 100 s and exposed to 1.4 V for 360 s. A previous study explained that, under the reverse current condition, upon start/stop cycles, the cell could experience voltage as high as 1.4 V [17]. Thus, it was reported that 1.4 V pulse cycling is suitable for an accelerated test to examine the cell degradation in automotive conditions (especially reverse current conditions) [15]. The pulse cycle was conducted 20 times at a cell temperature of 65 °C. The RHs of hydrogen and air were both 100%.

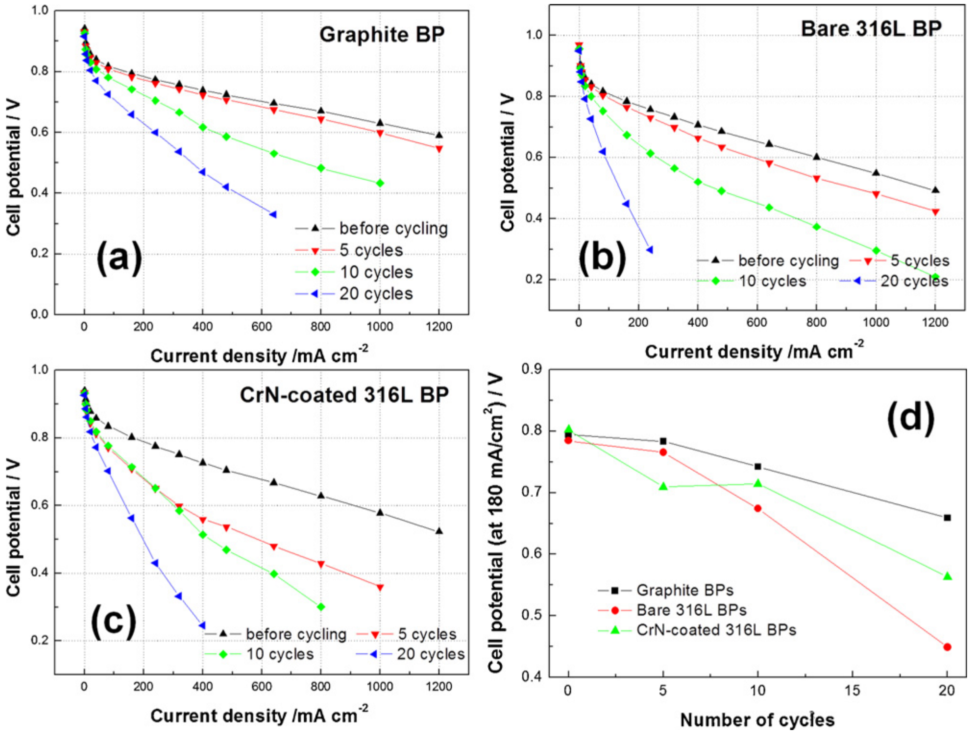

Fig. 2. Effects of 1.4 V pulse cycling on the *i–V* curves for the single cells employing (a) graphite, (b) bare 316L, and (c) CrN-coated 316 L BPs. (d) Cell voltage at 160 mA cm^{-2} as a function of the cycle number.