# Surface modification of stainless steel bipolar plates for PEMFC (proton exchange membrane fuel cell) application

**Young-Hoon Yun · Sung-Churl Choi**

**Abstract** Stainless steel 316 and 304 plates were deposited with a metallic film (top layer) and a conductive oxide film (intermediate layer) by a sputtering method and an E-beam method, respectively. The conductive oxide film was formed on the stainless steel plates in the range of thickness of 200, 400, and 600 nm. The XRD patterns of the conductive oxide films showed a typical indium-tin oxide (ITO) crystalline phase. The metallic films of 100 nm thickness were subsequently formed on the surface region of the bare stainless steel plates and the stainless steel plates deposited with ITO thin film. Surface morphologies of the stainless steel bipolar plates deposited with conductive film and metallic film were observed by AFM and FE-SEM. The metallic films on the stainless steel plates represented the microstructural morphology of the fine columnar grains of 10 nm diameter and 60 nm length. The electrical resistivity and contact angle of the stainless steel bipolar plates modified were examined as a function of the thickness of the conductive oxide film.

**Keywords** Proton exchange membrane fuel cell (PEMFC) · Bipolar plate · Conductive oxide film · Metallic film · Resistivity

Y.-H. Yun (✉)
Department of Hydrogen & Fuel Cell Technology,
Dongshin University,
252 Daeho,
Naju Jeonnam 520-714, South Korea
e-mail: yunh2@dsu.ac.kr

S.-C. Choi
Department of Advanced Materials Science Engineering,
Hanyang University,
Seoul 133-791, South Korea

## 1 Introduction

Proton exchange membrane (PEM) fuel cells show relatively low working temperature, a high efficiency, a high power density and a rather rapid response to the load variation, thus it is applied to FCEVs (fuel cell electric vehicles), submarines and a distributed power generation system using directly hydrogen gas or through reforming natural gas [1–3]. Wide application range in power generation system of PEMFCs is also due to some advantages in weight as well as dimension compared to other fuel cell stack types. In present, the fabrication and commercialization of PEMFC stack and its major components are very important for the utilization in several power generation systems, especially new generation of vehicle programs and such hydrogen-powered fuel cell vehicles [4–7].

Generally, PEM fuel cell technologies are closely related to polymer electrolyte membrane, metallic catalyst, balance of plant (BOP) and bipolar plates. Above all, the cost and weight of manifold bipolar plates in PEMFC are the chief obstacles to commercialization. The present bipolar plates for PEMFCs are the machined, very thick and heavy graphite blocks [6]. The manifold graphite bipolar plates in the present PEMFC system would occupy large dimensions, weight fraction over 70–80% as well as fabrication cost of 40–45% [8–10].

As the alternative bipolar plate materials, carbon composites and metallic plates have been developed for PEMFC application [4, 11]. The metallic bipolar plates have several advantages of low cost fabrication and mass production as well as small thin plate. The development of the metallic bipolar plates such as stainless steels requires the prevention of the corrosion in acidic condition and the low surface energy or relatively high contact angle. The

protective film and conductive film have been considered for the maintenance of electrical properties and stability of metallic bipolar plates in PEMFCs [12–14].

In this study, the stainless steel 304 and 316 plates were deposited with the conductive oxide film and the metallic film. The metallic film and transparent conductive oxide (TCO) film were used to introduce the beneficial effects of the electrical conductivity and corrosion resistance for the multi-film deposited stainless steel bipolar plates. The deposition process of the conductive oxide film and metallic film for the metal bipolar plates was carried out by sputtering method and E-beam method. The crystal phases of the SUS plates deposited and the bare stainless steel plates were identified with the XRD patterns. The electrical resistivity of the bare stainless steel and the stainless steel plates modified with the conductive oxide film and metallic film were measured. Surface morphologies of the bare stainless steel and the SUS plates deposited were observed by SEM and AFM. The contact angle of the stainless steel bipolar plates modified was measured.

## 2 Experimental procedure

The surface regions of the stainless steel 304 and 316 plates (20 mm × 20 mm × 2 mm) were deposited with the transparent conductive oxide (TCO) such as an indium-tin oxide and a metallic film. The coating processes of the conductive oxide film and metallic film on stainless steel plates were carried out by a sputtering method (Vacuum Science Co. Korea) and an E-beam method (Electron Beam Evaporator, World Science Co., Korea). The multi-film deposited stainless steel bipolar plates consisted of a metallic film of approximately 100 nm thickness and an indium-tin oxide film (interlayer) of 200–600 nm thickness. The thickness of the conductive film was controlled by the deposition conditions such as the gas partial pressure ratio ($Ar/O_2$) and the deposition time. The deposition processes of the metallic film and the conductive oxide film were carried out under the conditions of the $10^{-6}$ Torr vacuum (operation time: 100 nm/15 min) and the $10^{-4}$ Torr vacuum (operation time: 200 nm/30 min), respectively. The heat treatment of the films was carried out by a RTA (rapid thermal annealing, MTP, USA) instrument. The crystalline phases of the films deposited on the stainless steel plates were confirmed with X-ray diffractometer (Xpert PRO, PAnalytical, The Netherlands). The electrical resistivities of the stainless steel plate deposited with conductive film and metallic film was measured through a two-point probe method using a $I$–$V$ sourcemeter (Keithley, USA). Surface morphologies of the multi-film deposited stainless steel plates were observed by scanning probe microscopy (XE-

200, PSIA corp. Korea) and field emission scanning electron microscopy (FE-SEM, JSM 6700F, JEOL, Japan). The water contact angles of the multi-film deposited stainless steel plates were measured by a contact anglemeter (Digidrop, GBX, France).

## 3 Result and discussion

### 3.1 XRD patterns of the multi-film deposited stainless steel bipolar plates

Figure 1(a) and (b) show the XRD patterns of the surface region of the stainless steel 304 and stainless steel 316 bipolar plates deposited with the transparent conductive oxide (TCO) film and the metallic film and the as-received stainless steel plates. All the multi-film deposited steel plates showed a typical γ-Fe phase pattern based on the SUS plate. The conductive oxide film and metallic film,



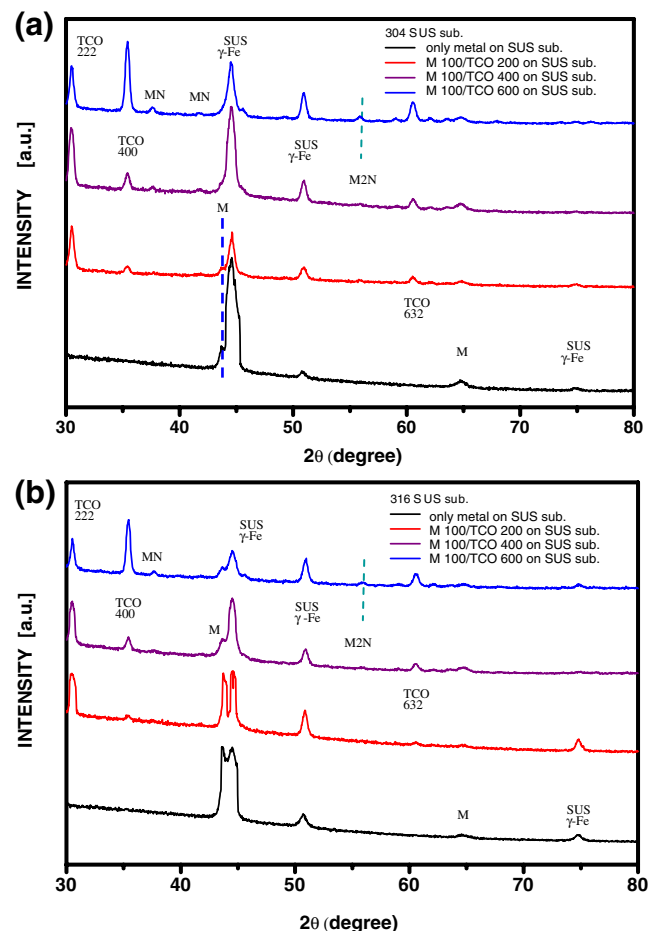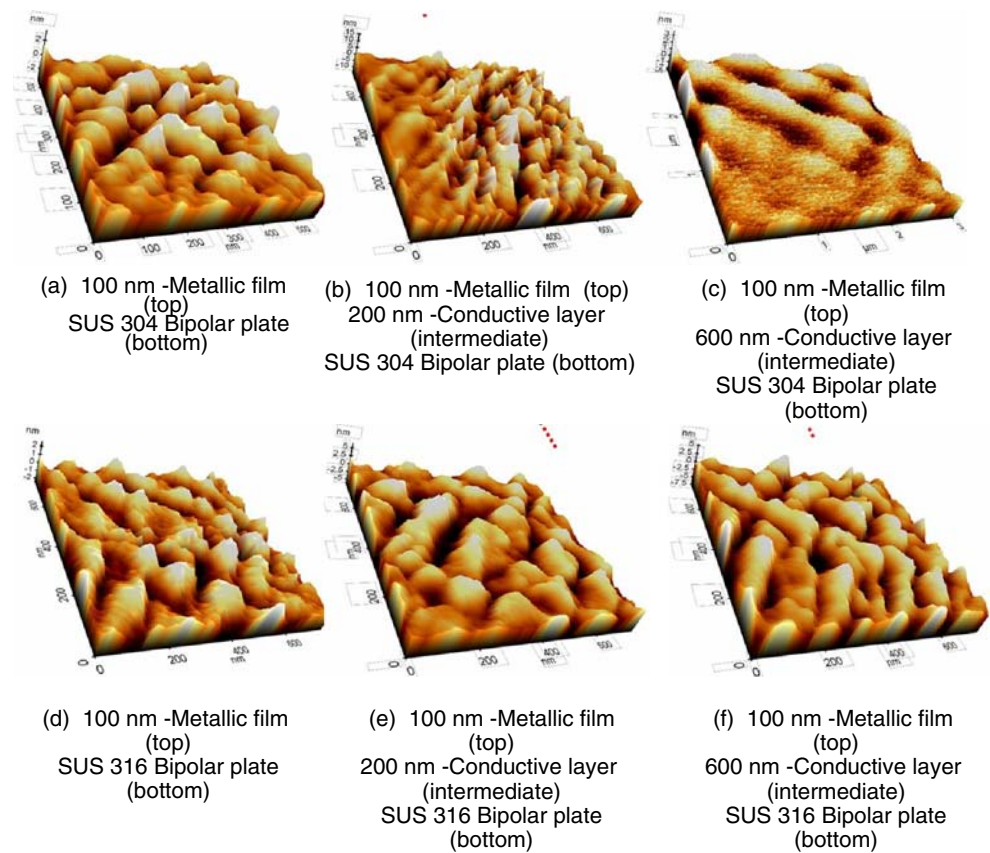Fig. 1 XRD patterns of metallic film [M: 100 nm] and conductive film [TCO: 200–600 nm] on stainless steel (a) 304 and (b) 316 plates

Fig. 2 AFM images of conductive film and metallic film coated bipolar plates



(a) 100 nm -Metallic film (top)
SUS 304 Bipolar plate (bottom)

(b) 100 nm -Metallic film (top)
200 nm -Conductive layer (intermediate)
SUS 304 Bipolar plate (bottom)

(c) 100 nm -Metallic film (top)
600 nm -Conductive layer (intermediate)
SUS 304 Bipolar plate (bottom)

(d) 100 nm -Metallic film (top)
SUS 316 Bipolar plate (bottom)

(e) 100 nm -Metallic film (top)
200 nm -Conductive layer (intermediate)
SUS 316 Bipolar plate (bottom)

(f) 100 nm -Metallic film (top)
600 nm -Conductive layer (intermediate)
SUS 316 Bipolar plate (bottom)

deposited on the stainless steel plates, showed a typical indium-tin oxide pattern and a chromium metallic pattern. The XRD patterns of the multi-film deposited stainless steel 304 and 316 plates represented some differences of peak intensities and peak width of the SUS $\gamma$-Fe and the TCO phases. Also, the multi-film deposited bipolar plates indicated the presence of the crystalline metal nitride phase. It was inferred that the chromium nitride compounds such as MN or $M_2N$ of the external surface were created by the heat treatment of the chromium film deposited on the SUS plates [11]. The external metal nitride films covered on the stainless steel plates could be related to the chemical stability and the surface characteristics of the stainless steel bipolar plates modified.

3.2 Surface morphologies of the multi-film deposited stainless steel bipolar plates
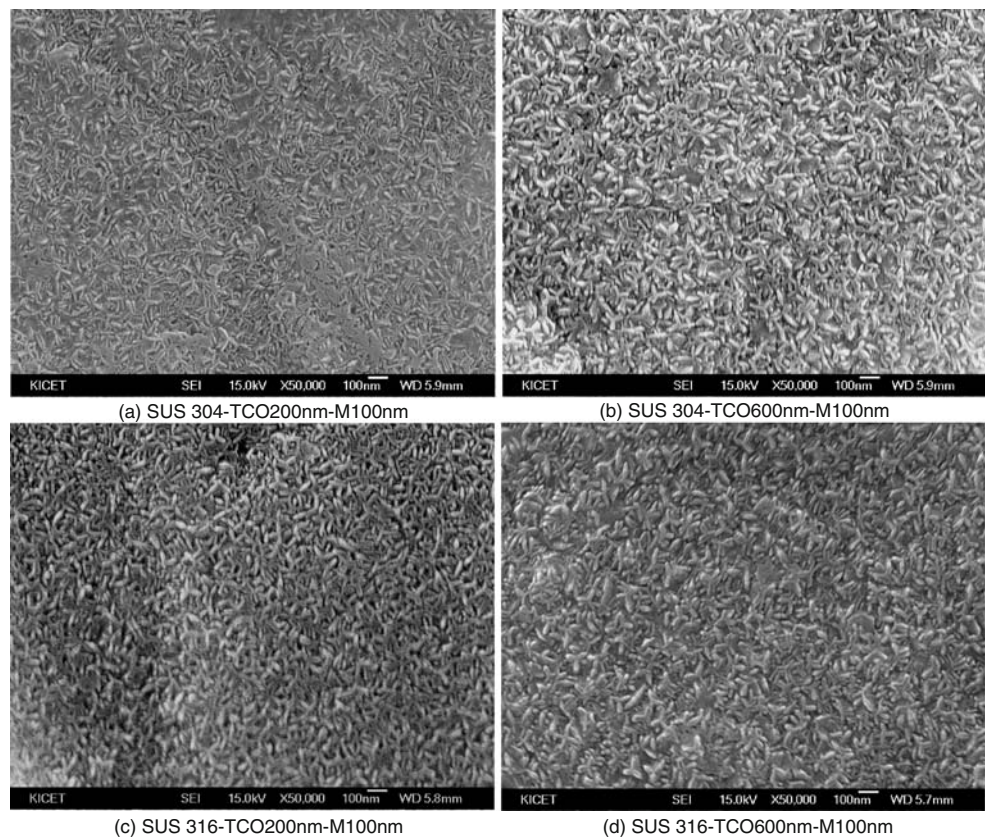
Figure 2 shows AFM surface morphologies of the SUS bipolar plates deposited with the chromium metallic film and the conductive oxide film. AFM images showed somewhat roughness variations according to the thickness of the TCO film on stainless steel plates. The surface roughness values of the multi-film deposited stainless steel 304 and 316 plates were shown in Table 1. The lowest roughness value of the multi-film deposited stainless steel bipolar plates was 0.389 nm. The roughness of the SUS bipolar plates increased with the thickness of the transparent conductive oxide film. Figure 3 shows FE-SEM images of the SUS bipolar plates deposited with the metallic film and conductive oxide film. The external metallic films formed on the SUS plates demonstrated the microstructural morphology of the columnar grains regardless of the presence of the intermediate conductive film. The fine columnar grains of the external surface showed relatively a uniform shape of approximately 10 nm diameter and 60 nm length throughout the entire region of the specimens. These

Table 1 Surface roughness of stainless steel 304 and 316 bipolar plates deposited with external metallic film and transparent conductive oxide (TCO) film

| Surface structure | Roughness (Ra) | |
|---|---|---|
| | SUS 304 bipolar plate (nm) | SUS 316 bipolar plate (nm) |
| 100 nm metal | 4.805 | 4.316 |
| 100 nm metal / TCO 200 nm | 5.520 | 5.665 |
| 100 nm metal / TCO 400 nm | 14.590 | 13.430 |
| 100 nm metal / TCO 600 nm | 0.389 | 6.379 |

**Fig. 3** FE-SEM images of metallic film [M] and conductive film [TCO] coated-SUS 304, 316 plates



(a) SUS 304-TCO200nm-M100nm

(b) SUS 304-TCO600nm-M100nm

(c) SUS 316-TCO200nm-M100nm

(d) SUS 316-TCO600nm-M100nm

crystalline columnar grains showed the size variation according to the condition of the film formation and the interlayer thickness.

### 3.3 Current–voltage characteristics of the deposited-stainless steel bipolar plates

Figure 4 shows the current–voltage characteristics of the bare-SUS 304, 316 plates and the multi-film deposited stainless steel plates. The I–V characteristics of the multi-film deposited bipolar plates showed rather a rapid change compared to the bare-SUS plates. The bare stainless steel 304 and 316 plates showed resistivity of approximately 2 and 7 Ω cm, respectively. The multi-film deposited SUS bipolar plates showed the resistivity of approximately 10 Ω cm. The stainless steel 304, 316 bipolar plates, which were modified with the only metallic film by E-beam method, showed relatively low resistivity of about 5 and 6 Ω cm, respectively.

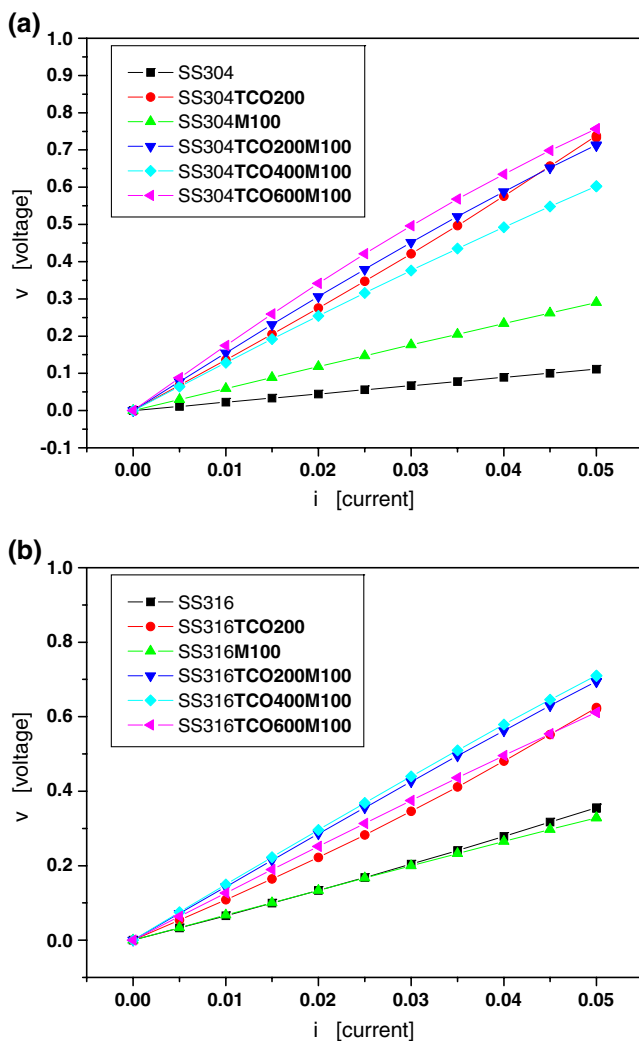### 3.4 Contact angles of the multi-film deposited-SUS bipolar plates

Figure 5 shows the contact angles of the bare stainless steel plates and the bipolar plates deposited with the metallic film and the conductive film. The bare-SUS 304, 316 plates showed approximately 60° and the stainless steel bipolar plates modified with two materials showed the contact angle of about 80° and 90°. Contact angle of the bipolar plates in PEM fuel cell is very important in an effective drainage or a circulation of water created during cell operation [4]. The bipolar plates for PEM fuel cell application require a high contact angle and a low surface energy. The stainless steel bipolar plates deposited with only the metallic film showed relatively high water contact angle (lower surface energy) compared to that of the bare-SUS plates. It seemed that the stainless steel plates deposited with the only metallic film showed the lower surface energy or the higher water contact angle. The presence of the intermediate conductive film would affect the external surface morphologies or the surface roughness of the metallic bipolar plates. Therefore it could be inferred that the water contact angle or the surface energy of the metallic bipolar plates containing the intermediate conductive layer were changed according to the external surface morphologies or the surface roughness.
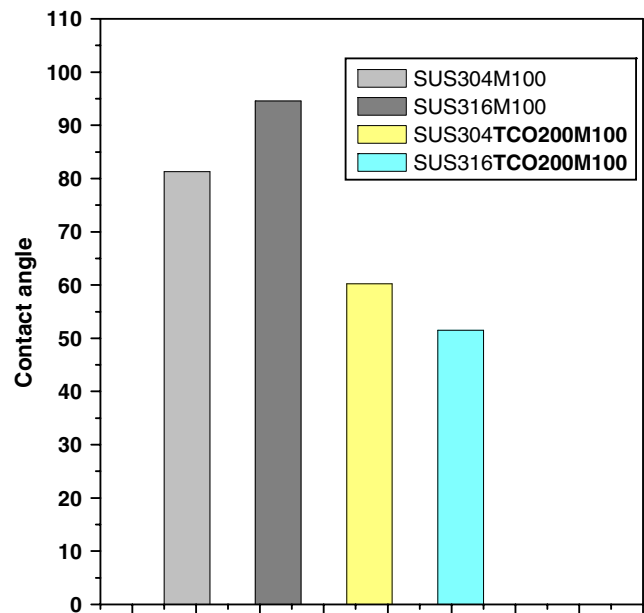
## 4 Conclusion

The stainless steel bipolar plates for PEMFC application has been modified with the metallic film by an E-beam

method and the conductive oxide film by a sputtering method. The thickness of the conductive oxide film and metallic film were approximately 200–600 and 100 nm, respectively. The XRD patterns of the SUS plates modified showed typical crystalline phases of the metallic film and conductive film as well as SUS substrate. The columnar grains of the external surface region were observed in FE-SEM images of the multi-film deposited specimens and showed the size variation according to the deposition thickness of the intermediate films. The multi-film deposited bipolar plates modified with conductive film and metallic film showed resistivity of approximately 10 Ω cm. The stainless steel 316 plate deposited with the chromium metallic film showed a similar behavior to the current–voltage characteristics of the bare stainless steel plates. The stainless steel bipolar plates modified with two



**Fig. 5** Contact angles of metallic film [M: 100 nm] conductive film [TCO: 200 nm] coated-SUS plates

films showed rather a high contact angle compared to the bare stainless steel plates. For enhancing the electrical properties and corrosion resistance of the stainless steel bipolar plates, other metallic films such as titanium and gold or very thin ITO film under 50 nm thickness would be used in further investigation.

**Fig. 4** (**a**) *I–V* characteristics of metallic film [M: 100 nm] conductive film [TCO: 200–600 nm] coated-SUS 304 plate. (**b**) *I–V* characteristics of metallic film [M: 100 nm] conductive film [TCO: 200–600 nm] coated-SUS 316 plates

## References

1. V. Mehta, J.S. Cooper, Review and analysis of PEM fuel cell design and manufacturing J. Power Sources. **114**, 32–53 (2003)
2. P. Coatamagna, S. Srinivasan, Quantum jumps in the PEMFC science and technology from the 1960s to the year 2000: Part I. Fundamental scientific aspects J. Power Sources. **10**, 242–252 (2001)
3. F. Barreras, A. Lozano, L. Valino, C. Marin, A. Pascau, Flow distribution in a bipolar plate of a proton exchange membrane fuel cell: experiments and numerical simulation studies J. Power Sources **144**, 54–56 (2005)
4. A. Hermann, T. Chaudhuri, P. Spagnol, Bipolar plates for PEM fuel cells: a review Int. J. Hydrogen Energy **30**, 1297–1302 (2005)
5. E.A. Cho, U.-S. Jeon, S.-A. Hong, I.-H. Oh, S.-G. Kang, Performance of a 1kW-class PEMFC stack using TiN-coated 316 stainless steel bipolar plates J. Power Sources **142**, 177–183 (2005)
6. S. Joseph, J.C. Mcclure, R. Chianelli, P. Pich, P.J. Sebastian, Conducting polymer coated stainless steel bipolar plates for proton exchange membrane fuel cells (PEMFC) Int. J. of Hydrogen Energy **30**, 1339–1344 (2005)

7. H. Tsuchiya, O. Kobayashi, Mass production cost of PEM fuel cell by learning curve Int. J. Hydrogen Energy **29**, 985–990 (2004)
8. R. Blunk, M.H.A. Elhamid, D. Lisi, Y. Mikhail, Polymeric composite bipolar plates for vehicle applications J. Power Sources. **142**, 177–183 (2005)
9. X. Li, I. Sabir, Review of bipolar plates in PEM fuel cells: flow-field designs Int. J. Hydrogen Energy **30**, 359–371 (2005)
10. J. Huang, D.G. Baird, J.E. McGrath, Development of fuel cell bipolar plates from graphite filled wet-lay thermoplastic composite materials J. Power Sources **150**, 110–119 (2005)
11. M.P. Brady, K. Weisbrod, I. Paulauskas, R.A. Buchanam, K.L. More, H. Wang, M. Wilson, F. Garzon, L.R. Walker, Preferential thermal nitridation to form pin-hole free Cr-nitrides to protect proton exchange membrane fuel cell metallic bipolar plates Scr. Mater. **50**, 1017–1022 (2004)
12. N. Kazufumi, Y. Eiichi, G. Hisaaki, H. Kazuhito, U. Makoto, O. Hideo, S. Yasushi, K. Teruhisa, M. Toshihiro, N. Junji, Solid polymer electrolyte fuel cell, European patent "EP 1 094 535 A1"
13. J. Wind, R. Späh, W. Kaiser, G. Böhm, Metallic bipolar plates for PEM fuel cells J. Power Sources **105**, 256–260 (2002)
14. S.-H. Wang, J. Peng, W.-B. Lui, Surface modification and development of titanium bipolar plates for PEM fuel cells J. Power Sources. **160**, 485–489 (2006)