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Proton Exchange Membrane Fuel Cell Bipolar Plate Analyses by GD-OES and Raman

Application
Note

Multitechniques
GD-RA-01

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Abstract: Bipolar plates are key components of proton exchange membrane fuel cells – they notably distribute fuel gas and air and conduct electricity. Various materials and surface treatments have been developed to improve their properties. Here, we described a reverse engineering study on a bipolar plate from a commercial vehicle using GD-OES and Raman spectroscopy. The analyses revealed that the plate had an amorphous carbon coating on a titanium base plate.

Keywords: Proton exchange membrane fuel cell, bipolar plate, GD-OES, Raman spectroscopy

Introduction

Fuel cells are devices that generate electricity by a chemical reaction of hydrogen and oxygen. They don't emit greenhouse gas as by-products. Therefore, they are key assets for clean energy. Among the many types of fuel cells, the proton exchange membrane fuel cell (PEMFC) is already used a lot as an alternative to combustion engines in automotive. Bipolar plates are one of the main components of PEMFC (Figure 1), as they need to connect each cell, assure conduction from cell to cell, and prevent electrolyte leakage.[1] Therefore, the bipolar plates are required to have excellent electrical and thermal conductivities, gas impermeability, good mechanical properties, and efficient drainage of excess water.[1] To meet all these requirements, many researchers have dedicated their efforts to develop various plate materials and surface treatments to improve their properties.

Glow discharge optical emission spectrometer (GD-OES) is an elemental analytical technique used for fuel cell bipolar plates.[2-6] It provides direct elemental depth profiles from surface to substrate without the need to cross-section. GD-OES' unique features are fast analysis and multiple element detection down to hydrogen. Raman spectroscopy is a chemical analysis technique, which can characterize chemical structure and crystallization of a material non-invasively. It is notably used for characterization of carbon coating materials in bipolar plates analyses.[6-9]

In this note, we carried out material identification of a fuel cell bipolar plate used in a commercial automotive by GD-OES and Raman spectroscopy.

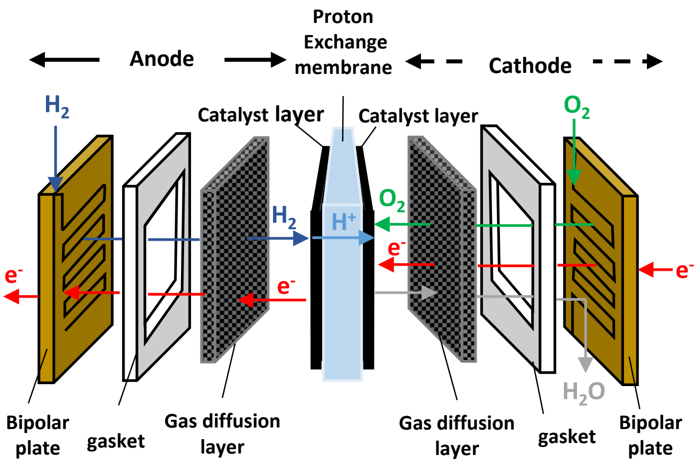

Figure 1. The structure of proton exchange membrane fuel cell.

Table 1.Previous studies using GD-OES and Raman spectroscopy for PEMFC bipolar plate analysis

	Reference	Base	Surface Treatment	GD-OES	Raman
[2]	Barranco et al. (2010)	Al-5083	CrN	✓	
[3]	Ouyang et al. (2020)	Ti	NiP-TiN coating	✓	
[4]	Park et al. (2014)	Ni	Cr-coating	✓	
[5]	Shironita and Umeda (2019)	SUS445	Nitriding treatment	✓	
[6]	Chung et al. (2008)	SUS304	Carbon coating on Ni coating	✓	✓
[7]	Jang and Lee (2015)	SUS316L	Diamond-like carbon coating		✓
[8]	Che et al. (2020)	SUS316L	Amorphous hydrogenated coating		✓
[9]	Show (2007)	Ti	Amorphous coating		✓

Sample information

We got bipolar plates disassembled from a proton exchange membrane fuel cell coming from a commercial automotive. Figure 2 shows the bipolar plate (anode side) analyzed in this application note. The full size of the plate was 425 mm x 147 mm and the surface looked bronze in color. We trimmed a piece of this bipolar plate (Figure 2b) for GD-OES analysis. Surface was not flat requiring the use of a dedicated mounting.

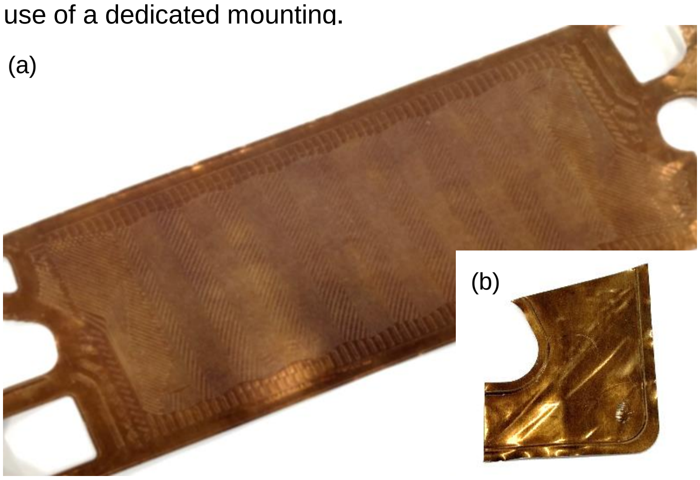

Figure 2. (a) The bipolar plate analyzed in this application note. (b) The edge area of the bipolar plate was cut into a small piece for GD-OES analysis

Experiment 1- Screening analysis using GD-OES

We used HORIBA GD-Profiler2™ glow discharge optical emission spectrometer (Figure 3a), which provides fast and simultaneous analysis of all elements of interest. The operation involves the controlled sputtering of a representative area of a sample to be analyzed by the glow discharge plasma and the simultaneous optical emission observation of the sputtered species.

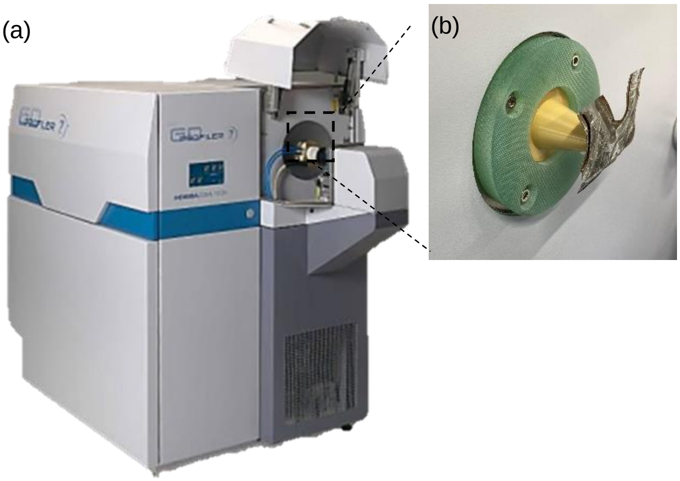

Figure 3 (a) HORIBA GD-Profiler2™ glow discharge optical emission spectrometer (b) Sample setting on elephant anode.

The GD-Profiler2™ is equipped with an RF source that can operate in pulsed mode to improve depth resolution for thin film analysis. We used a special 2 mm anode (called “elephant anode”, Figure 3b) for this analysis because of constraints in available flat surface area for the sample piece. The analysis was carried out under 600 Pa of Argon gas and 20 W with pulse sputtering of 1000 Hz and a duty cycle of 0.125.

Figure 4 shows the elemental depth profile performed on the bipolar plate. In this GD-OES profile, carbon (C) signal is clearly detected at the beginning of the sputtering time followed by titanium (Ti). The nitrogen (N) signal is confirmed to be at background level in Figure 4 which indicates that no leakage happened during the analysis. In the surface layer, hydrogen (H) is detected but mainly at the beginning of sputtering time. The H profile was different from the profile of carbon which suggest that the carbon coating was not hydrogenated (called C:H) like the one reported by Petry et al. (2016).[10] Regarding the base plate, some publications reported the use of titanium[3,9,11] and some reported titanium alloys such as Ti-6Al-4V.[12] Our GD-OES result clearly show the profile of titanium, but co-existing elements such as aluminum and vanadium were not detected. (The profiles of aluminum (Al) and vanadium (V) are not displayed in Figure 4 because their signals were at background level). The profile confirms that the base plate used here is titanium, not titanium alloy.

Through GD-OES analysis, we could therefore conclude that the bipolar plate consisted of carbon coating and a titanium base plate.

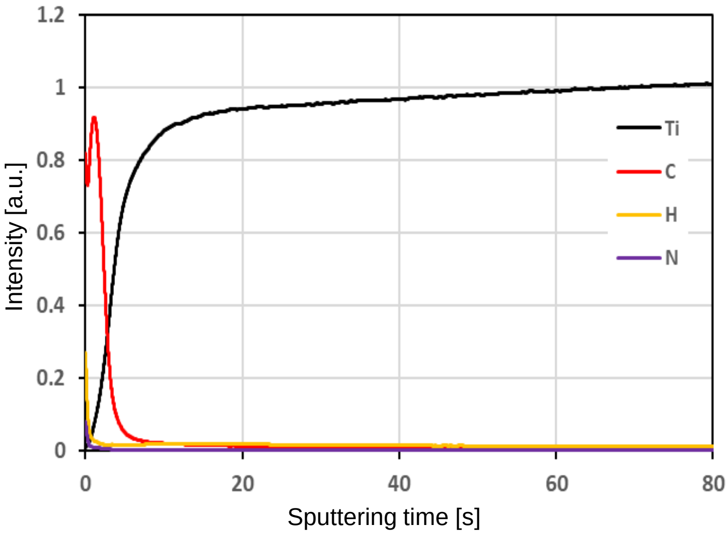

Figure 4. Elemental depth profile of the bipolar plate analyzed by GD-Profiler2™.

Experiment 2- Characterization of carbon coating using Raman spectroscopy

To identify the chemical structure of the carbon coating layer of the bipolar plate, we used the HORIBA LabRAM HR Evolution Confocal Raman Microscope (Figure 5a) to perform spectrum analysis. Raman spectroscopy can be used to examine substances with ordered and disordered crystal structures.[6-9] We analyzed the carbon coating of the disassembled plate with 100x objective lens and 532 nm laser with 10 % ND filter (6 mW at the sample). The 300 gr/mm of grating was used and the spectral range was set as 600 to 2200 cm^{-1} in order to cover both D-band and G-band. The acquisition time was set to 10 seconds with five repeat accumulations.

The Raman spectrum obtained from the carbon coating of the bipolar plate is shown in Figure 6; two peaks were found, namely D-band and G-band, respectively. The D-band, positioned around 1360cm^{-1}, is known to represent the sp^2 carbon breathing pattern in the ring structure. In addition, the D-band is active in the presence of defective and impure graphite structure.[8,9] On the other hand, the G-band located around 1580cm^{-1} is known to represent the stretching vibration of the sp^2 bond of carbon. Moreover, the G-band is active in the presence of an ordered material network composed of interconnected hexagonal carbon rings.[8] These two peaks are commonly observed in amorphous carbon coatings[6-9], and they could be found in our result. When we compared our result with a previous study on a similar bipolar plate material[9], the spectra shape in our result was closer to the amorphous carbon coating deposited at 500-600℃ than the one deposited at room temperature.

Through Raman analysis, we could identify the amorphous form of the carbon coating on our bipolar plate.

Figure 5. HORIBA LabRAM HR Evolution Confocal Raman Microscope.

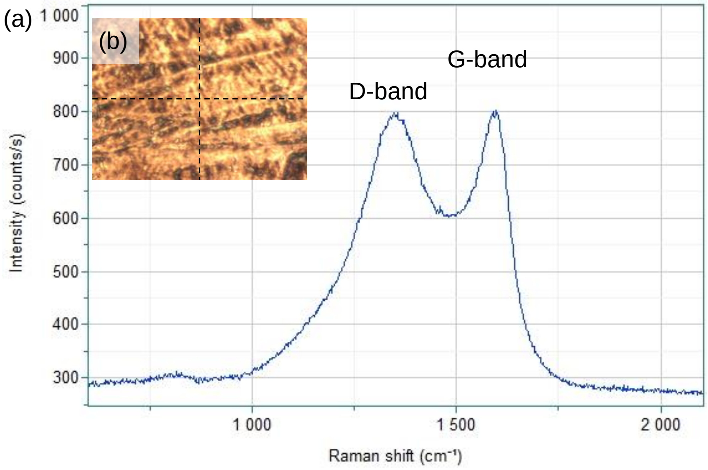

Figure 6. (a) Raman spectrum obtained on the carbon coated surface of the bipolar plate. (b) Optical image of the measurement area.

Conclusion

We analyzed an unknown bipolar plate disassembled from a commercial automotive fuel cell using HORIBA GD-Profiler 2™ and HORIBA LabRAM HR Evolution Confocal Raman Microscope. Without any prior knowledge of this bipolar plate, we were able to identify its composition as being a titanium plate covered with an amorphous carbon coating. The complementarity of techniques available at HORIBA provides a powerful solution for reverse engineering of fuel cell bipolar plates by material identification.

Acknowledgement

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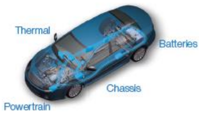

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