

Small, Thin-film Electric Potential Sensor for In-situ Evaluation of Fuel Cell Stack

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ABSTRACT

Measurement of electric potential is an effective means of monitoring changes in the characteristics of the materials used in fuel cells and of obtaining an understanding of the internal environments of the cells. In addition, measurement of the distribution of electric potential is important for the optimal design of fuel cells. However, it is necessary to supply hydrogen to conventional electric potential sensors to obtain a reference electric potential, and structural constraints limit the number of points at which they can be used for internal measurements. A new small, thin-film, self-hydrogen-generating sensor has been developed in order to address these issues. The new sensor can measure potential in any part of a fuel cell stack, and enables more accurate in-situ evaluation of the gas and water environments in the fuel cells.

1. Introduction

Development efforts are proceeding in the area of non-fossil fuel technologies, looking towards the realization of CO₂-free and zero emission motoring, in order to ameliorate environmental issues such as global warming and air pollution. As part of these efforts, Honda has developed a proprietary fuel cell stack that utilizes pure hydrogen as fuel.

Chemical reactions between hydrogen and oxygen in the fuel cells generate electricity, in addition to water as by-product. Figure 1 shows the configuration of a fuel cell. Fuel cells are composed of multiple micron-order layers: Bipolar plates, which serve as the gas flow paths, gas diffusion layers (GDL), which diffuse the gases to the electrodes, catalyst layers (CL), in which catalytic reactions are performed, and a proton exchange membrane (PEM)⁽¹⁾. Hydrogen at the anode electrode and oxygen at the cathode electrode react on the catalyst layers, generating a voltage in the cell. The movement of protons through the PEM and the movement of electrons generate electricity and water.

When utilizing fuel cells, it is necessary not only to attempt to secure the movement of ions and electrons and other electrical exchanges, but also to provide the cells

that supply reaction gases and water uniformly, and to promote the smooth expulsion of the water formed by the chemical reactions. However, it is challenging to confirm the status of gases and water in the microscopic space of the electrodes. Nevertheless, these reactions affect the performance of the fuel cells, so an accurate understanding of each environment and its function, and the formulation of designs on this basis, are vital to the realization of high-performance and high-quality fuel cells.

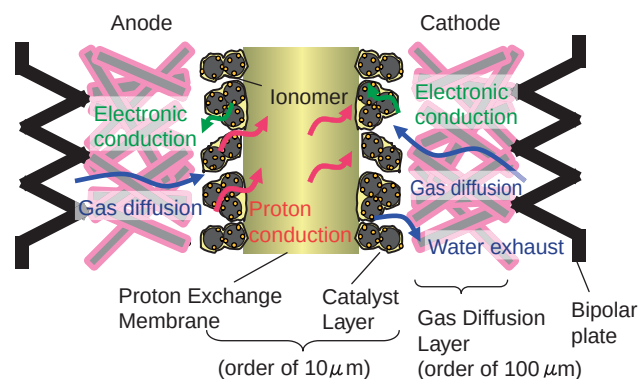


Fig. 1 Schematic of fuel cell

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2. Issues of Measurement of Potential Distribution in Fuel Cell Stacks

2.1. Necessity for Measuring Potential Distribution

Cell voltage is one of the parameters enabling an understanding of cell performance, but the status of the reactions in the cell cannot be accurately grasped from the cell voltage alone. To understand the internal status of fuel cells, therefore, research on a number of associated parameters is conducted, rather than just measuring cell voltage. Measuring potential is one way to estimate the status of the catalyst and gas environments. Also, recently, the number of reports looking at this parameter for assessing the deterioration of fuel cell materials and understanding the reaction environment inside the cells has increased.

Fuel cells are used under a variety of operating conditions, including start-up, shutdown, and air purge. In each of these states, declines in generation performance due to changes in the characteristics of the materials can be observed. Figure 2 shows a transmission electron microscope (TEM) photograph of the electrode catalyst of a fuel cell that had been put through a start-stop cycle, as an example of a change in material characteristics. The photograph shows that the Pt grain diameter is larger on the gas outlet side than the gas inlet side. Enlargement of the Pt grain diameter may lead to a decline in the activity of the catalyst, and is one factor that may cause a decline in cell performance. The distribution of changes like this in the characteristics of the cell materials is an effect of the distribution of potential (which results mainly from differences in environments, such as the gases and water in the electrodes), and is thought to affect the durability of the fuel cells⁽²⁾.

To enable a high operating voltage to be obtained, automotive fuel cell stacks are formed from layered stacks of several hundred fuel cell units (single cells). Because of this, variations occur in parameters including gas distribution, water discharge, and temperature environments in different areas of the stack, and this results in differences in potential.

The fact that the environment inside the fuel cells is

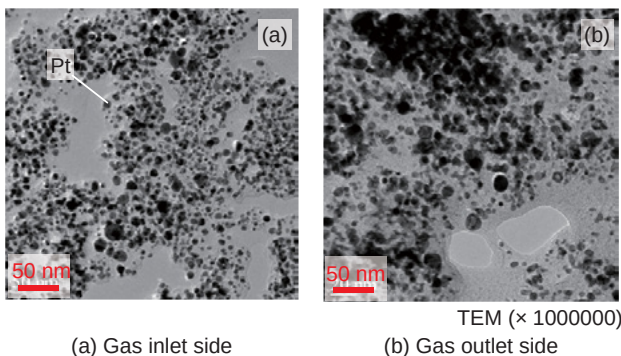


Fig. 2 TEM image of catalyst after start-stop cycle

not uniform makes it challenging to obtain an accurate understanding of the internal environment of the cells by measuring a potential in one area of the stack. Therefore, it is crucial in fuel cell stack design for the distribution of potential at multiple sites to be monitored, to allow the internal environment of the cells to be better understood.

2.2. Issues of Conventional Potential Measurements

Figure 3 shows a single fuel cell, used in conventional measurements of potential. A Pt foil or wire is positioned close to the hydrogen inlet flow path, and this is made the reference electrode for potential. The equilibrium potential of the adsorption and dissociation reaction of hydrogen on the surface of the Pt is considered to be 0 V, the reference potential, and the difference in the potential in the measured area against the reference potential is the environmental potential. Because of this, the reference electrode is termed a reversible hydrogen electrode (RHE) (Fig. 4)^{(3),(4)}. However, several issues exist in relation to these potential measurements using RHE reference: First, the reference potential cannot be maintained without a continuous supply of fresh hydrogen to the reference electrode; second, the distance of the reference electrode from the desired actual points for potential measurements will increase; and third, due to these reasons, errors may increase in measurements. When RHE is used, it is necessary to supply hydrogen to the position of the reference electrode, and the position of the reference electrode and the area for potential measurements should be close. Given these limitations on

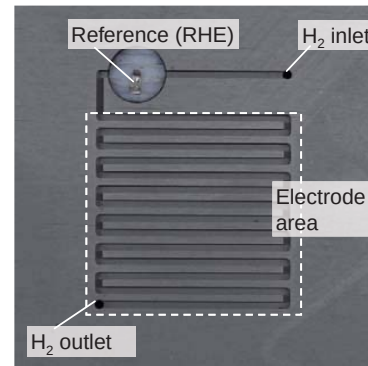


Fig. 3 Example of fuel cell with RHE

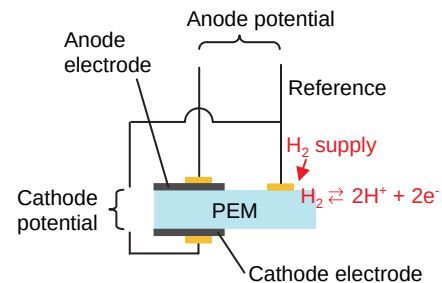


Fig. 4 Schematic of RHE

the positioning of the reference electrode and measurement conditions in conventional potential measurements, the majority of reports on this method focus on comparatively small single cells for testing use.

In addition, when the hydrogen used for power generation is also used for the reference electrode, the reference electrode needs to be placed close to the hydrogen gas inlet (upstream), based on the first RHE measurement issue discussed above (Fig. 3). In order to extend the range of potential measurements further toward gas outlet side of the cell or to another location, it is necessary to use a special gas line to the reference electrode⁽⁵⁾, but this is impractical method in an actual stack.

Introducing reference electrodes to a cell can also cause gas leaks and affects the actual generation reaction, which is counter to the purpose of using the electrodes. As this discussion indicates, numerous issues should be addressed in relation to potential measurements in fuel cell stacks.

3. Aims in Development of Small, Thin-film Potential Sensors

In order to overcome the issues discussed in Chapter 2, and to measure potential at any part of a fuel cell stack, it was necessary to miniaturize the measurement system used in the conventional method, including the reference electrode and the measurement section by integrating them into a sensor. Research was conducted with the following conditions established for the sensor:

- (1) Configuration of reference electrode
 - No requirement for fresh hydrogen supply for reference electrode
 - Provision of reference electrode with a hydrogen-generating section, because measurements should also be conducted when the stack is not generating
- (2) Shape of sensor
 - No interference with generating environment: Status close to that of actual operation (No major reduction in generating area, no impediment to gas flow)
 - The thickness of the sensor should not cause seal performance to decline, for prevention of leaks around the structure used for retrieval of the sensor
- (3) Sensor materials
 - No changes in materials such as deformation or contamination of generating environment (hot water, low-pH environment)
 - Good insulation and withstand voltage

4. Results of Application of Small, Thin-film Potential Sensor

4.1. Development of Potential Sensor

Figure 5 shows the external appearance of the small,

thin-film potential sensor when it is introduced to the membrane electrode assembly (MEA). The sensor incorporates a reference electrode and electrodes for measurement of potential, and is integrated by a thin film that supports these electrodes. This configuration enables the sensor to measure potential at any insert location.

A liquid crystal polymer (LCP) is used as the material for the film, due to its strong resistance to hot-water and acidic environments. Patterning the electrodes and the lead sections on the film realizes a sensor thin enough not to affect seal performance and increase electrical resistance. In addition, a multi-layered structure has been employed in order to help ensure a withstand voltage by maintaining the distance between the sensor electrodes.

The sensors are positioned on both sides of the CL that sandwich the PEM, and are covered by the GDL. In order to help prevent interfering with generation in the fuel cells, the sensor was designed to assure that it would occupy only a minimal area on the CL and maintain a stable reference potential.

A dynamic hydrogen electrode (DHE), which produces hydrogen from water by electrolysis, has been employed as the reference electrode (Fig. 6). This hydrogen-producing reference electrode necessitates the use of a separate power source for electrolysis, but it offers the advantage of enabling measurements to be taken when no hydrogen is supplied, for example when the stack is soaked or just before start-up, and it can thus measure potential in virtually all the environments occurring in fuel cells.

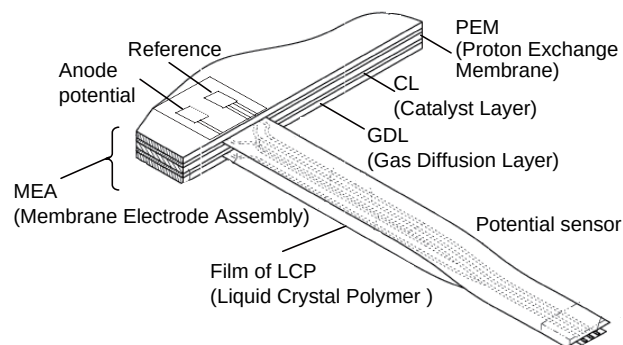


Fig. 5 Configuration of potential sensor

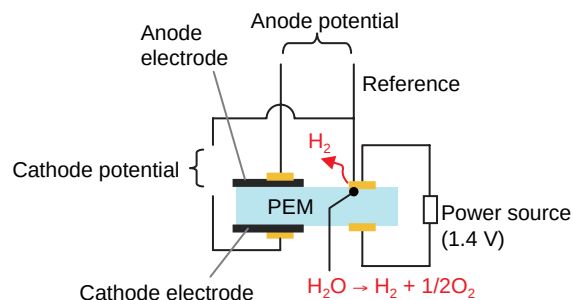


Fig. 6 Schematic of DHE

Table 1 Anode potential under H₂ and air condition

No	Anode potential (V)	
	H ₂ condition	Air condition
1	0.01	1.06
2	0.00	1.03
3	0.00	1.07
4	0.01	1.05

*At 25°C, atmospheric pressure, 100% RH

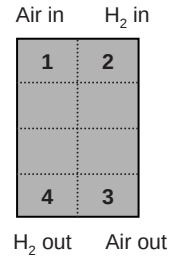
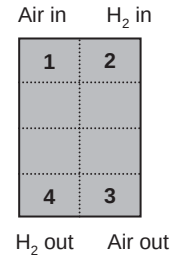


Table 2 Relation between difference of cathode and anode potential and cell potential

No	Potential (V)			
	(a) Anode	(b) Cathode	(c) (b)-(a)	(d) Cell
1	-0.01	0.79	0.80	0.79
2	0.00	0.80	0.80	
3	-0.01	0.79	0.80	
4	-0.01	0.78	0.79	

*At 25°C, atmospheric pressure, 100% RH



4.2. Verification of Functioning of Potential Sensor

The following method was used to confirm whether the new sensor would accurately measure potential. Sensors were positioned at eight points on MEA, from the gas inlet side to the gas outlet side. Cathode potential and anode potential at each of these points and cell voltage were measured (Fig. 7).

The reference electrode is expected to display a stable reference potential under any conditions. RHE-type reference electrodes require a constant supply of the hydrogen used for power generation in order to maintain a stable potential, but DHE-type reference electrodes produce a reference potential using hydrogen produced by water electrolysis. Because of this, the electrode should accurately show 0 V for anode potential in each measurement position, whether or not there is a supply of hydrogen for generation. In addition, the difference

between the anode potential and cathode potential in each measurement position should match the cell voltage.

First, the anode potential was measured in the electrode at the inlet and outlet sides in a hydrogen environment and an air environment in order to verify the reference potential. The measurement results are shown in Table 1.

The measurements under a hydrogen environment were all basically 0 V, while the measurements under an air environment were all basically 1 V (close to the oxidation-reduction potential of oxygen), indicating that the reference electrode was functioning properly.

The difference in potential between the anodes and cathodes and the cell voltage during generation were also measured and verified. The results of these measurements are shown in Table 2. The differences in potential between the anodes and cathodes basically match the cell voltage, indicating that the potential measurements are correct.

4.3. Measurement of Distribution of Potential Using the Potential Sensor

Figure 8 shows the measurement results of the potential distribution in a single actual cell. In order to make the graph easier to read, only representative data for the inlet and outlet sections is shown. Low-stoichiometry and high-moisture operating conditions were employed during the measurements in order to produce a large difference in the potential distribution.

The respective potentials change in response to the generating load. As the load becomes higher, the potential distribution in the electrodes changes significantly, and the

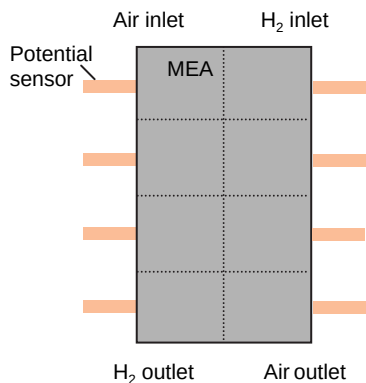


Fig. 7 Layout of potential sensor

anode potential at the outlet side increases. It is conjectured that this increase in the potential of the anode side occurs as a result of the fact that the level of hydrogen diminishes and the level of water produced increases in proportion to the proximity to the outlet side, and submersion therefore occurs due to flooding. The results show that it was possible to measure the potential distribution within the electrodes.

4.4. Results of Application in a Fuel Cell Stack

Figure 9 shows the measurement results of the potential distribution at start-up. If some time has elapsed since the stack was shut down, the hydrogen in the anode is consumed, and an air environment forms in both electrodes. At start-up, air and hydrogen are mixed at the anode side. The internal potential distribution follows the flow of hydrogen (shown by the arrow). The potential of the opposed electrode, the cathode, becomes high, with its maximum potential exceeding 1.4 V under certain conditions. The high potential is maintained for the longest period close to the outlet, where gas exchange is slow. This result matches the results of the analysis of changes in material characteristics discussed above. A certain control system is needed in order to prevent high potential. The consideration of changes in potential has, as outlined above, rendered the flow of gases in the cell

visible, and might thus provide important suggestions for the design of flow paths that increase the efficiency of gas substitution, and the design of materials possessing high withstand potential.

Figure 10 shows the measurement results of potential distribution during the air purge to the anode electrode immediately following stack shutdown. Similar to the results for measurement during start-up, the potential distribution follows the flow of air within the anode (shown by the arrow), and a high potential is generated on the cathode side. The potential is highest on the inlet side, and this also matches the results of the analysis of changes in material characteristics.

In addition, the potentials at different layers within the stack (Fig. 11) before start-up differ, layer by layer. This indicates that the gas environment and concentration within the stack differs with soak time. This data is important in extending the life of fuel cells by controlling the stack shutdown procedure or applying the design considerations to gas manifolds.

The reference electrodes in general use for potential measurements (the RHE discussed above) require a supply of hydrogen, and therefore cannot be used for measurement of potential when a stack is shut down and hydrogen is not being supplied. However, the new sensor is a self-hydrogen generating type, and thus offers the

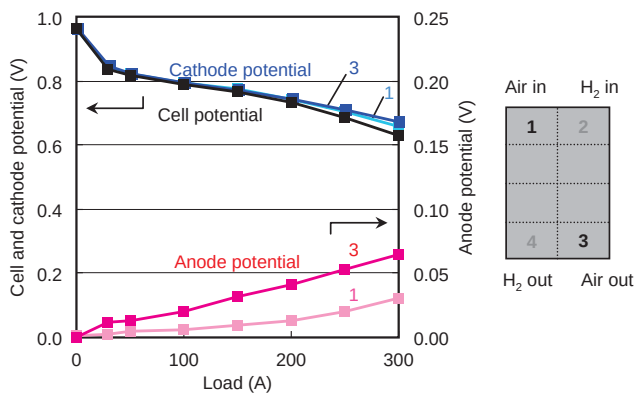


Fig. 8 Potential distribution during generation

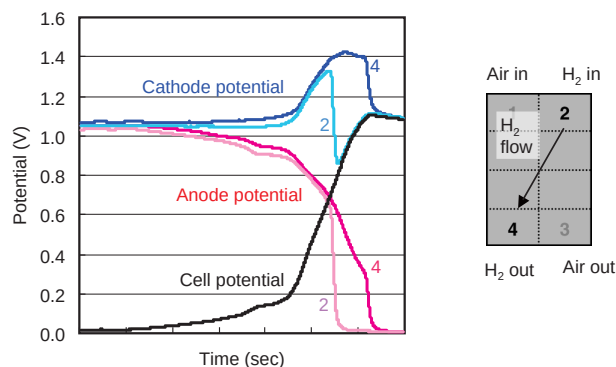


Fig. 9 Potential distribution at start-up

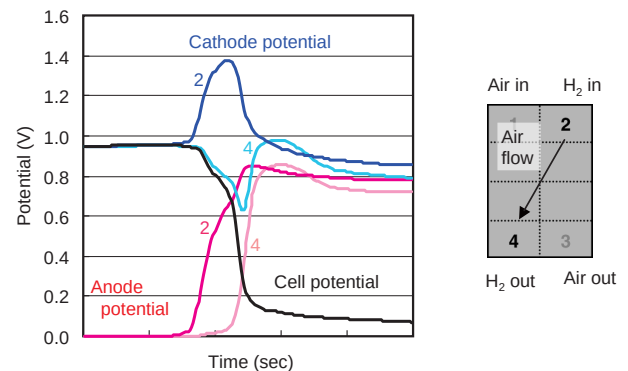


Fig. 10 Potential distribution at purge

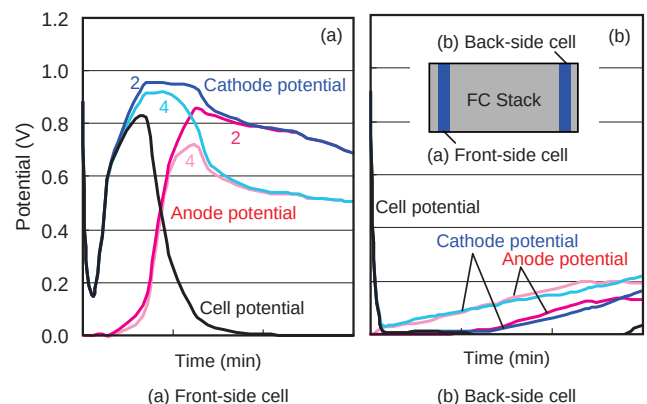


Fig. 11 Potential distribution before start-up

advantage of enabling measurements to be taken in an environment without hydrogen supply (when the stack is shut down).

5. Conclusion

An original potential measurement sensor has been developed, enabling measurements of the potential distribution in the cells and the differences in environmental conditions between the different layers in the actual fuel cell stack, which previously were not possible. The confirmation experiment indicates the effectiveness of this sensor as a strong tool in fuel cell development, such as when attempting to understand changes in material characteristics and the generating environment in fuel cells.

- (1) The development of a small, thin-film potential sensor able to self-generate hydrogen has enabled potential measurements to be taken in virtually all operating environments, and has also enabled measurements to be taken in an actual fuel cell stack, which previously represented a challenge.
- (2) The new sensor has enabled detailed measurements, in an actual fuel cell stack, of the potential distribution in the electrodes and the potential distribution due to the position of the cell in the stack, which previously could not be accurately evaluated, and has clarified the relationship between potential distribution, areas of electrode deterioration, and changes in the characteristics of the cell materials under a variety of operating conditions.
- (3) Tests demonstrated that the sensor displays a high degree of versatility, able to be used for measurements in a single cell and an entire fuel cell stack.

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