고분자전해질 연료전지용 전극물질의 빠른 스크리닝을 위한 멀티셀 테스트 시스템에서 개별셀의 성능편차에 대한 분석

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Analysis for Performance Deviation of Individual Cells in a Multi-Cell Test System for Rapid-Screening of Electrode Materials in PEMFCs

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ABSTRACT

A multi-cell test system with 25 independent cells is used to test different electrode materials simultaneously for polymer electrolyte membrane fuel cells (PEMFCs). Twenty-five segmented membrane electrode assemblies (MEAs) having the same or different Pt-loading are prepared to analyze the performance deviation of cells in the multi-cell test system. Improvements in the multi-cell test system are made by ensuring that the system performs voltage sensing for the cells individually and inserting optimum gaskets between the MEAs and the graphite plates. The cell performances are improved and their deviations are significantly decreased by these modifications. The performance deviations changed according to various cell configurations because the operating conditions of the cells, such as the gas flow and concentration, differed. This cell system can be used to test multiple electrodes simultaneously because it shows relatively uniform performance under the same conditions as well as linear correlation with various catalyst loadings.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been studied as alternative sources of power

because they produce little or no pollutants such as carbon monoxide, and nitrogen oxide compounds. However, PEMFC systems have not yet been commercialized because of their high production cost, which is attributed to the fact that some of their components are very expensive. Platinum (Pt), which is one of the expensive materials that is used in the production of PEMFCs, has been used as an electrocatalyst in the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR). Many researchers have conducted studies to explore the possibility of new elements other than Pt as electrocatalysts and have tried to find suitable elements that can assist Pt in accelerating the electrochemical reactions in a fuel cell[1-5]. In light of these facts, it can be said that the quantity of Pt used in the PEMFC system should be reduced in order to facilitate the commercialization of this system. However, it should be noted that a large amount of time and money will be required to procure appropriate catalysts which usually be tested in the cell. Therefore, it is essential to develop a high throughput system based on combinatorial chemistry to rapidly screen different catalysts.

To the our knowledge, Mallouk's group has proposed a fast screening method based on combinatorial chemistry for finding appropriate electrocatalysts, which they prepared electrode arrays containing 715 unique combinations of five elements (Pt, Ru, Os, Ir and Rh) to be used as catalysts for oxygen reduction and water oxidation reactions in regenerative fuel cells[6,7]. In their fuel cell system, pH indicators were used in the electrolyte solution to detect the concentration of protons that could be produced and eliminated by electrochemical reactions. Woo's group used a similar method and reported novel quaternary Pt-based electrocatalyst containing Pt, Ru, Mo,

and W, for methanol oxidation reaction (MOR)[8]. Jiang and Chu developed an electrolyte-probe screening method, for combinatorial electrochemical analysis; this method involved the use of a movable electrolyte probe with reference and counter electrodes, and an array of working electrodes[9]. Next, Liu and Smotkin developed an array membrane electrode assembly(MEA) for the high throughput screening of direct methanol fuel cell (DMFC) electrocatalysts; their system adheres to all of the abovementioned rules[10,11]. It should be noted that an MEA is the most essential component used for the screening of electrocatalysts. This MEA consists of a polymer electrolyte membrane (e.g. Nafion) sandwiched between a standard catalyzed fuel cell carbon diffusion backing on one side, and an array of catalyzed diffusion backing discs on the opposite side. This fuel cell system consists of 25 independent fuel cell electrodes with a common counter electrode. A number of studies have used the array fuel cell system for the screening of DMFC anode catalysts[12]. However, most of these studies have focused on screening electrocatalysts for DMFCs and not PEMFCs.

In this study, we use a multi-cell system similar to that developed by Smotkin's group. Further, we evaluate the performance deviation of each of the 25 individual cells in a PEMFC system under the same conditions and try to reduce its deviation by amending cell configuration and others. In addition, we show the possibility of rapidly screening electrocatalysts by controlling the individual fuel cell using a multi-channel potentiostat.
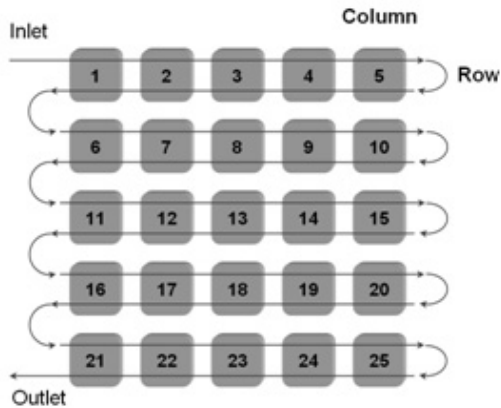
2. Experimental

2.1 MEA Preparation

The electrode and MEA were prepared by con-
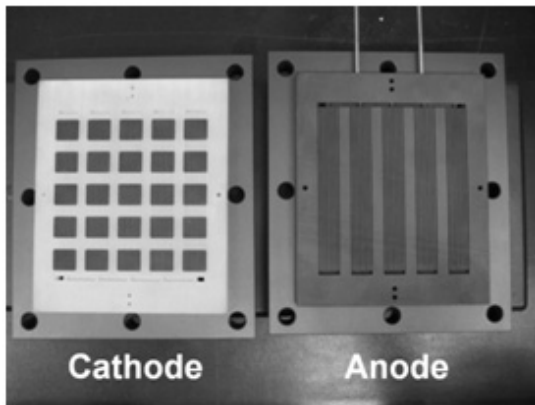
(a)

(b)

Fig. 1 (a) Pictures of multi-cell frames, and (b) Gas flowing route and segmented electrode numbering

ventional methods described in many literatures[13-16]. The catalyst, 20% Pt/C (HiSPEC 3000, Johnson Matthey Fuel Cell), was mixed with water and isopropyl alcohol (IPA). The mixture was then ultrasonically stirred for 30min, and then, 5% Nafion ionomer solution (DuPont) was added to the mixture in ratio of 70: 30 (Pt/C: Nafion); the resulting solution was again ultrasonically stirred for 30min. Subsequently, the solution as catalyst ink was sprayed onto the wet-proofed carbon paper (AvCarb P50T, Ballard) using an auto-spray machine at 70°C until Pt loading reached 0.35

mg/cm^2. The anode size was 11x11 cm^2 and the cathode was cut into 25 pieces, with each electrode size measuring 1.5x1.5 cm^2. The MEA was prepared by sandwiching the membrane, pretreated Nafion 115, between the anode and cathode, and hot-pressing them at 120°C under 200 bar for 2 min.

2.2 Fuel Cell Test

The home-made cell frame used for testing and the configuration of segmented electrodes are shown in Fig. 1 (a). To measure the individual current at the segmented cells, the gas flow plate in the cathode side specially designed. The 25 segmented small graphite blocks with gas flow channel was fixd in an epoxy plate. The MEA was set between a graphite plate for anode and a segmented plate for cathode. This cell was operated by home-made test station that consisted of gas/temperature control units and a multichannel potentiostat (WonAtech, WBCS3000). Gas flow rates for H_2 and O_2 were set at 400 cc/min and 250 cc/min, respectively. H_2 and O_2 gases were humidified by a heating humidifier at 70°C and 65°C, respectively. The gas flowing route is shown in Fig. 1(b). Cell temperature was maintained at 60°C for the duration of the test. For testing the cell performance, voltage was decreased with the step of 0.05V or swept at the scan rate of 0.05 mV/s from open circuit voltage (OCV) to 0.3 V, and the current densities were recorded auto-matically. Cyclic voltammetry (CV) was carried out to characterize the segmented electrodes electrochemically while hydrogen gas was supplied to the anode side and nitrogen gas was used to purge the cathode side. Voltage was swept 30 times, and then, the final scan was collected to obtain precise information for the adsorption properties of hydrogen and oxygen on the Pt
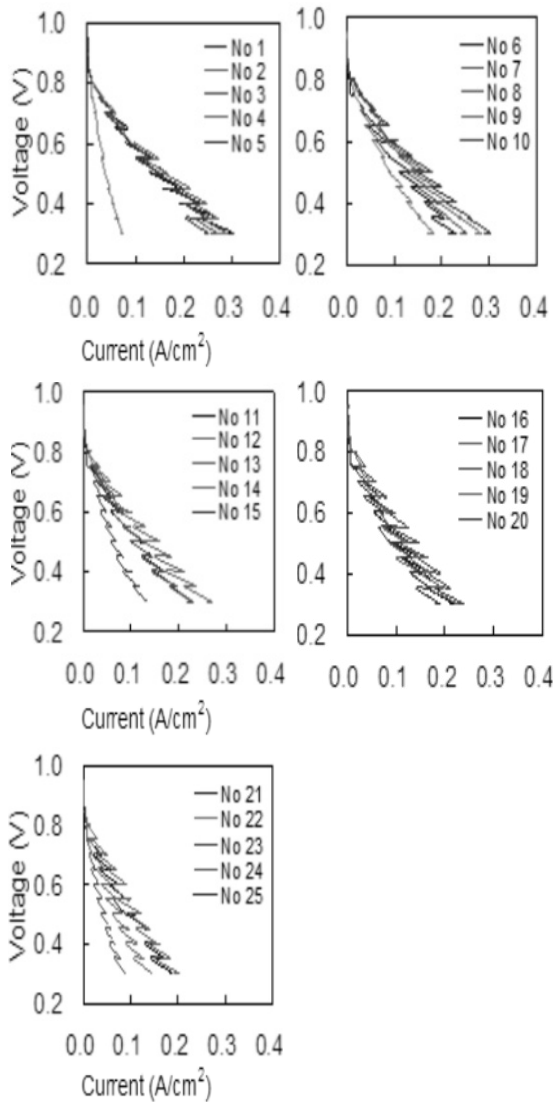
Fig. 2 Polarization curves of multi-cell system by linear voltage sweep with the step of 0.05V from OCV to 0.3V. Each step was maintained for 30 second

Fig. 3 Comparison with the current density of each cell at different voltage

surface[17].

3. Results and discussion

3.1 Cell performance deviation

As above mentioned that the segmented electrodes

were prepared and tested under the same conditions, they should show the same performance. Fig. 2 and Fig. 3 show the polarization curves and current distributions of each cell at different cell voltages, respectively, which were recorded for every 0.05 V increase from OCV to 0.3 V. The performances of each electrode located in the rows decreased gradually toward at the gas outlet. However, the current densities of all the electrodes were very low and the average value at 0.5 V was around 0.13 A/cm^2, even when pure hydrogen and oxygen were used. The performance deviation between the segmented electrodes was very high and increased at lower voltages. Some of the individual electrodes showed very poor performance, such as cell number 2, 7, 15, and 24. The poor performance may be attributed to the poor electrical connection between the electrode and the current collector (the graphite block with the gas channel), and uneven gas distribution.

The CV test was also performed in order to determine the electrochemical surface area and to elucidate the adsorption properties of reactant species on Pt surface. Fig. 4 shows the CV curves
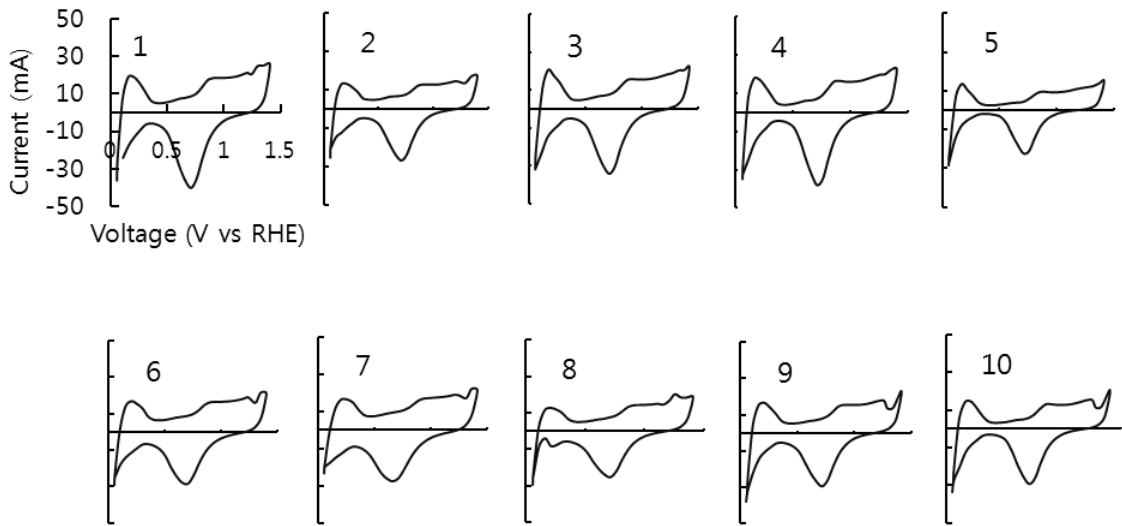
Fig. 4 Cyclic voltammograms from cell number 1-10. Voltage range and scan rate: 0.04-1.4 V and 25 mV/s

of cell number 1–10. Each curve shows the typical adsorption/desorption of hydrogen and oxygen on the Pt electrode[18]. This implies that each cell is electrochemically active and its catalysts are well connected to the ionomer and carbon, both ionically and electrically. As shown in Fig. 4, the peak intensities (or currents) are slightly different for each cell. The coulombic charges for desorption

Fig. 5 Coulombic charge for hydrogen and oxygen desorption calculated from CV results

of hydrogen and oxygen, which were calculated from the CV test, are shown in Fig. 5[19]. A comparison of Figs. 3 and 5 shows that there is no correlation between the adsorption charge and the cell performance. As seen in cell numbers 2, 8, 12, 13, 17, 22, and 25, the charge values for adsorption of H_2 and O_2 are high whereas for cell numbers 1, 3, 4, 9, 10, and14, high peak densities were not observed. Both the charge values assigned to H_2 and O_2 should be similar to each other because the same amount of Pt was loaded on the anode and cathode. However, a high deviation is observed in the CV curves.

The electric connection between the electrode and the current collector was examined to solve the low performance. Cell voltages of all the electrodes were detected by setting another probe (voltage sensing) in array cell testing frame. Setting two probes, one for current and the other for voltage, on current collector could remove voltage drop by ohmic loss induced from the electric resistance between the current collector
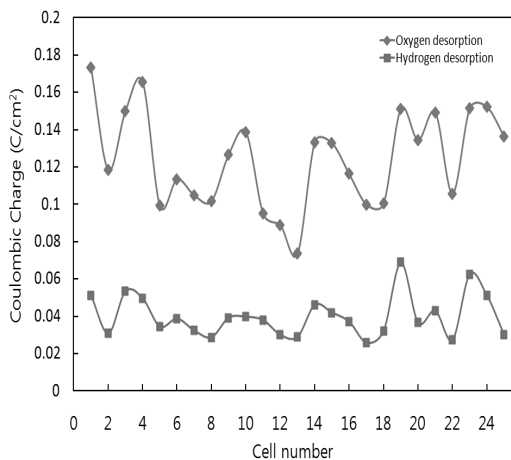
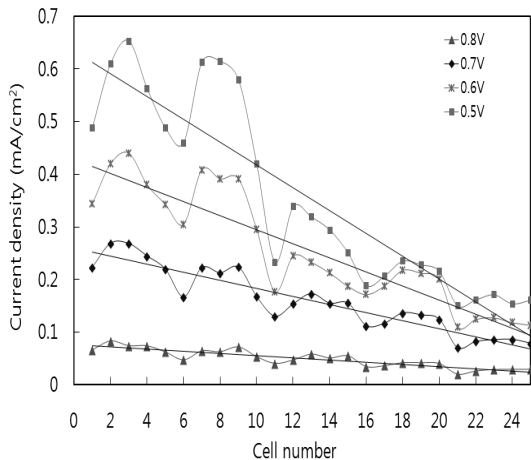Fig. 6 Comparison of current density at different voltage (after setting voltage-sensing probes)

Fig. 7 Comparison of current density at different voltage (after improving gas diffusion)

(graphite block) and lead wire for current flow. After setting another voltage-sensing probe, the MEAs were tested under the same conditions, the results of which are shown in Fig. 6. As shown in this figure, cell performances significantly improved in the first (Cell No. 1-5) and second rows (Cell No. 6-10) as shown in Fig. 1, up to ~ 0.6 mA/cm^2 at 0.5 V. This proved that there was a problem with electrical connection between the electrode and the current collector, which did not allow accurate voltage sensing. However, the performance deviation sharply increased with the increasing cell numbers. In particular, the electrodes after the third row showed very poor performance. We assumed that these low performances were caused by uneven gas distribution. Thus, we changed the gasket between the graphite plate (separator) and the MEA, which separates each cell individually and promotes uniform gas flow.

A Teflon sheet was used as a gasket and inserted between the MEA and the anode graphite plate; a silicon gasket was inserted between the segmented MEA and the cathode graphite plate. The thickness of the MEA is approximately 500-
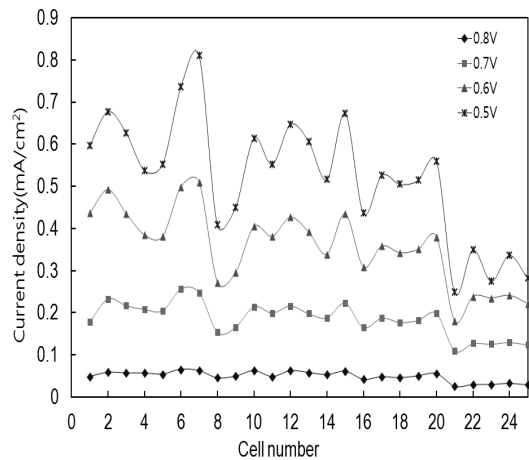
550 μm, and the Nafion membrane is approximately 125-130 μm; consequently, the thicknesses of both the cathode and anode are approximately 185-210 μm. We inserted the gasket between these interspaces to ensure the effective diffusion of gas over the catalysts where the electrochemical reactions occurred. When the gaskets were changed to improve gas distribution, the cell performance increased considerably 1st-4th row of the cells as shown in Fig. 7. However, the other cells that are located near the gas outlet still showed low performance implying that gas flow was not uniform from the inlet to the outlet. We supposed that the performance deviation of each cell could be induced by the location of the cell because the concentrations of the gas and the vapor were different at the inlet and the outlet.

3.2 Data Analysis

Smotkin's group, the first to develop an array fuel cell system, reported that they adopted optimum cell configuration, called as the Latin square arrangement, to minimize systematic errors because
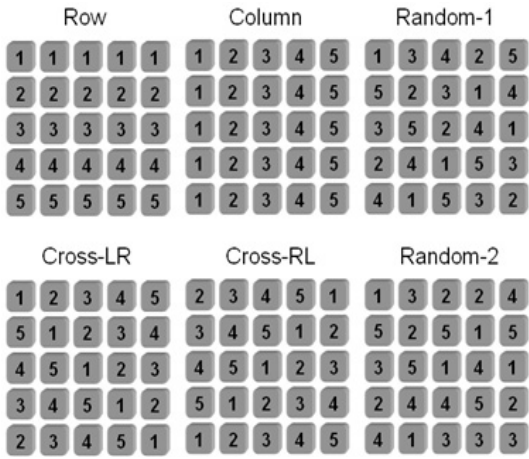
Fig. 8 Various cell arrangements in 25 segmented MEA

the array electrodes used in the system showed a certain amount of performance deviation[20]. They found a performance deviation of ~10% for individual cells in the H_2/air fuel cell system for a current less than 10 mA/cm^2 of current. However, in our system, the measured current was quite high, and the current fluctuation was also severe as compared to Smotkin's results. Moreover, NuVant Systems, the first manufacturer of array fuel cell system, presented that performance deviation data varied more according to the cell configuration, even if the cell current range was with in 100 mA/cm^{2}[21]. Also, other experiment using segmented bipolar plate with current density distribution device showed similar results to ours[22].

In order to minimize the performance deviation induced by the location of the cell in our system, different types of cell arrangements were used for data acquisition, as shown in Fig. 8 and the cell performances according to cell configuration are shown in Fig. 9. As shown in this figure, performance deviation varies among the six types of arrangements, even when the Pt loadings were the same. The data selected from the column,
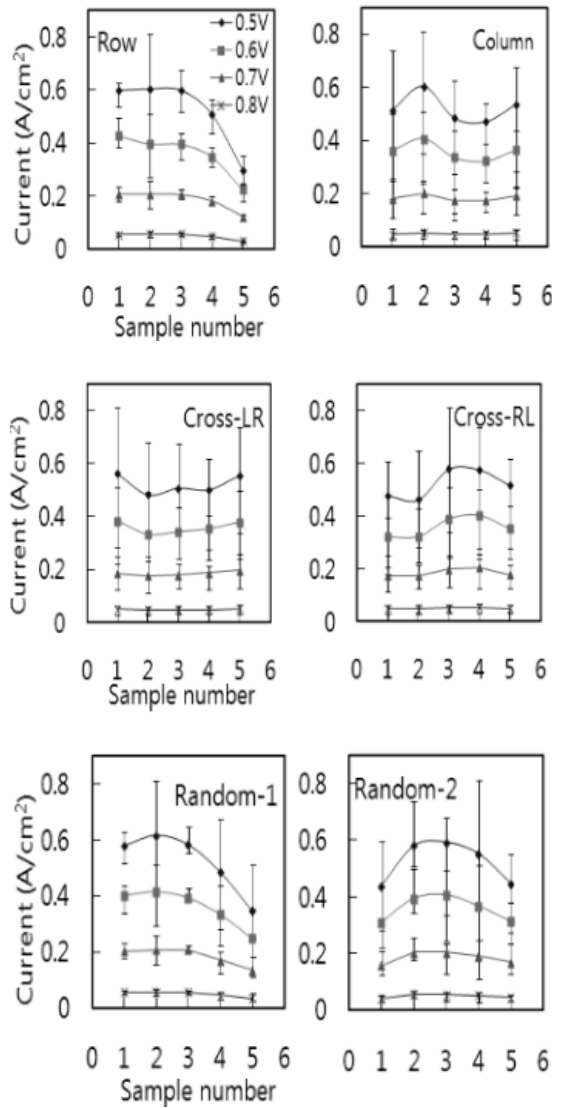

Fig. 9 Comparison of cell performances in various cell arrangements

cross-LR and cross-RL arrangement shows better uniformity than that selected from the row and two random configuration arrangement. In particular, the cells selected from cross-LR arrangement show the best uniformity. This implies that the arrangement of the 25 multi-cell system in the cross-LR arrangement minimizes performance
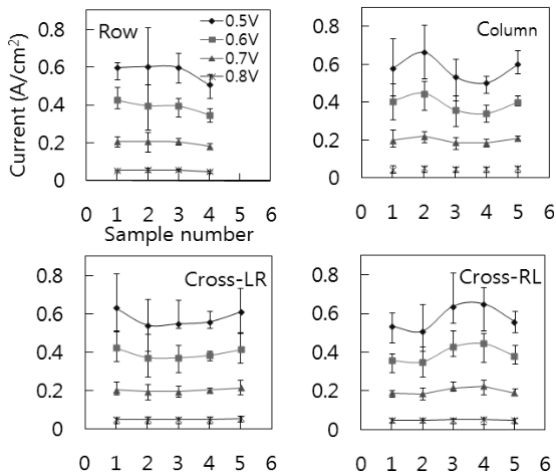
Fig. 10 Comparison of performances in various cell arrangements without last row of multi-cell, which was replotted from Fig. 9
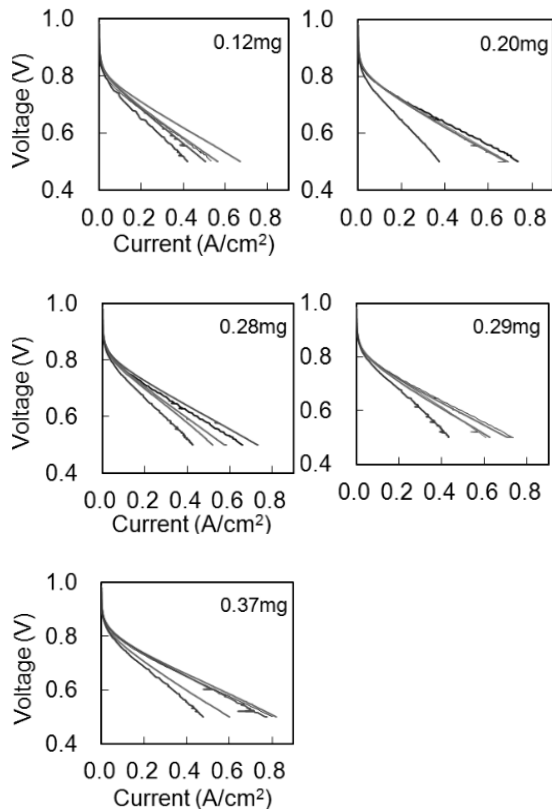

Fig. 11. Polarization curves of multi-cell using cross LR cell arrangement under different Pt-loading. Voltage sweep from OCV to 0.5V; scan rate of 0.05mv/s

deviation; consequently, analysis of the data obtained from this arrangement give a more accurate result. Incidentally, the data from the last row, which was collected from cell numbers 21-25, shows an abnormally lower performance than that collected from the other cells which might be caused by pressure drop around outlet[23]; therefore, we removed the data from cell number 21-25 and analyzed them again. Fig. 10 shows curves plotted to remove the data obtained from the last row from Fig. 9. From the x-error bar analysis, it was found that the shorter error bar that represented the data selected from all the rows other than last row showed less performance deviation.

Fig. 10. Comparison of performances in various cell arrangements without last row of multi-cell, which was replotted from Fig. 9.

3.2 Different Pt loading

An easy way to identify the difference in cell performance in a multi-cell system is to test cells by varying the Pt loading on the catalyst[24]. Fig.

11 shows the performance of each cell as a function of the amount of Pt loading used. These graphs were obtained from a slow voltage sweep with the scan rate of 0.05 mV/s. The cell performance increases with the Pt loading. The current distribution on Pt loading is plotted in Fig. 12 without using the data from the last row because the gas distribution problem still existed. The cell performances in Fig. 12 show good correlation with the change in Pt loading.

4. Conclusion

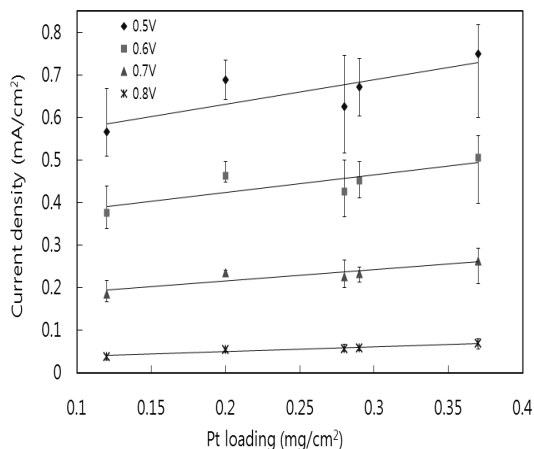The performance deviation among 25 cells in

Fig. 12 Comparison of performances in cross-LR cell arrangement without last row of multi-cell

multi-cell system was investigated for a PEMFC system. First, the problems associated with the connectivity between the electrodes and the gas channels, such as the electric resistance and the uneven gas distribution, were resolved by voltage sensing and improved gasket, respectively. The cell performance increased significantly; however, the performance deviation within the individual cells still existed. Different types of cell arrangement were adopted to process the data in order to minimize the performance deviation attributed to the cell location. It was found that the cross-LR cell arrangement showed the best uniform performance among the six types of arrangements. The cells with different Pt catalyst loading were analyzed to identify the variation in performance attributed to the cell arrangement. The cell performances linearly increased with an increase of Pt loading. From the above results, it was concluded that this multi-cell test system could be used for the rapid screening of catalyst materials.

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