

Short communication

Performance of proton-exchange membrane fuel cells using the catalyst-gradient electrode technique

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Abstract

For commercialization of proton-exchange membrane fuel cells (PEMFCs), stack fabrication cost should be significantly reduced, possibly by reducing the loading of platinum catalyst. Under normal operating conditions using humidified hydrogen and air, the performance of a single cell is not uniform over the active electrode area due to non-uniform distribution of reactant gases and water. To improve catalyst utilization, a catalyst-gradient electrode method is applied to a single-cell fabrication. This procedure is found to be very effective in reducing platinum usage without loss in cell performance.

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1. Introduction

The proton-exchange membrane fuel cell (PEMFC) is considered to be an efficient and clean energy-conversion system for stationary and automotive applications. For commercialization of PEMFCs, however, it is necessary to reduce the stack fabrication cost, possibly by decreasing the loading of Pt catalyst. To this end, many studies have been carried out [1–9]. Pt/C catalysts with Pt and a carbon support of diverse particle size have been employed to enhance Pt utilization by optimizing the electrode porosity. Several noble or non-noble metals and Pt-based alloys have been screened to replace the Pt catalyst. Diverse fabrication methods for membrane-electrode assemblies (MEAs) have been developed for efficient use of the Pt catalyst.

Most of the previous studies [1–9] have dealt with electrodes fabricated with a uniform structure and composition over the whole active area although it was revealed by current-distribution measurements and mathematical models that the current density of a PEMFC was dependent upon the relative position of the unit area in the flow-field [10–13]. In general, on

feeding humidified reactant gases, cell performance gradually decreases from the gas inlet to the gas outlet region since the reactant gases are rich in the former and depleted in the latter. Moreover, an increase in water vapour pressure downstream can impede mass transport to the catalyst of gas outlet region. Since the reaction is exothermic, there is an autocatalytic heating effect leading to a further increase in the reaction rate in the gas inlet region.

For efficient utilization of the whole electrode active area of PEMFCs, non-uniform gas-diffusion layers (GDLs) were applied in MEA fabrication [14,15]. Johnson et al. [14] demonstrated that the performance of a single cell could be improved by employing an in-plane, non-uniform, GDL composed of carbon cloth, carbon paper, grooved carbon paper and pierced carbon paper. The complexity in assembling these GDLs, however, makes the structure hardly applicable to stack fabrication. Chen et al. [15] showed that a graduated polytetrafluoroethylene (PTFE) water-management layer between the backing layer and catalyst layer could effectively prevent drying out of the electrolyte membrane and flooding of the cathode, which resulted in a high-performance PEMFC. On the other hand, since the PTFE layer acts not only as a hydrophobic agent but also as a binder for the carbon particles, carbon loss from regions with low PTFE content can cause performance degradation.

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In this study, to obtain a cell with uniform performance distribution over the whole active area, electrodes have been fabricated with a non-uniform distribution of catalyst loading. The catalyst loading is increased from the gas inlet to the gas outlet to counteract the depletion of reactants in the gas stream. Using this catalyst-gradient electrode technique, the Pt loading can be reduced without performance loss.

2. Experimental

2.1. Preparation of membrane–electrode assemblies and single cells

Catalyst ink was prepared by mixing 40 wt.% Pt/C (E-tek Inc.) with isopropyl alcohol (Baker analyzed HPLC Reagent) and then the mixture was ultrasonicated for 1 h. A 5 wt.% Nafion® solution (Du Pont Inc.) was added to the catalyst ink, which was ultrasonicated again for 1 h. The MEAs were prepared by the catalyst coated membrane (CCM) method, in which the prepared ink was sprayed over a Nafion® 112 membrane. The active electrode area was 25 cm². Single cells were assembled with the prepared CCMs, gas-diffusion media (Sigracet®, SGL Carbon Inc.), gaskets, and graphite blocks.

2.2. Characterization of membrane–electrode assemblies

Before assemble, the surface morphology of the catalyst-coated membrane was examined by means of scanning electron microscopy (Hitachi S-4200).

Hydrogen and air were fed to the anode and the cathode of the single cell after passing through bubble humidifiers held at a temperature of 80 and 65 °C, respectively. The cell temperature was 80 °C. The performance of the single cell was evaluated by measuring the current–voltage (*i*–*V*) characteristics with an electronic load (Daegil Electronics Inc., EL 1000P). The resistance of the single cell was determined by a.c. impedance with the air electrode as the working electrode and the hydrogen electrode as the reference and counter electrodes. An IM6 instrument (ZAHNER) was used for impedance measurements and the applied frequency was varied from 10 mHz to 10 kHz with an excitation voltage of 5 mV (peak-to-peak). In these studies, the counter electrode also served as a reference electrode, since the overpotential at the counter electrode for hydrogen oxidation or evolution reaction is negligible [16].

3. Results and discussion

3.1. Effect of anode catalyst loading on fuel cell performance

To reduce the anode catalyst loading, MEAs with anode catalyst loading in the range of 0.2–0.01 mg Pt cm⁻² were prepared while keeping the cathode loading constant at 0.4 mg Pt cm⁻². The data in Fig. 1(a) clearly show that a reduction in Pt loading from 0.2 to 0.03 mg Pt cm⁻² has little effect on cell performance. In the examined range of Pt loading, the difference in cell voltage at a current density is less than 7 mV if the current density

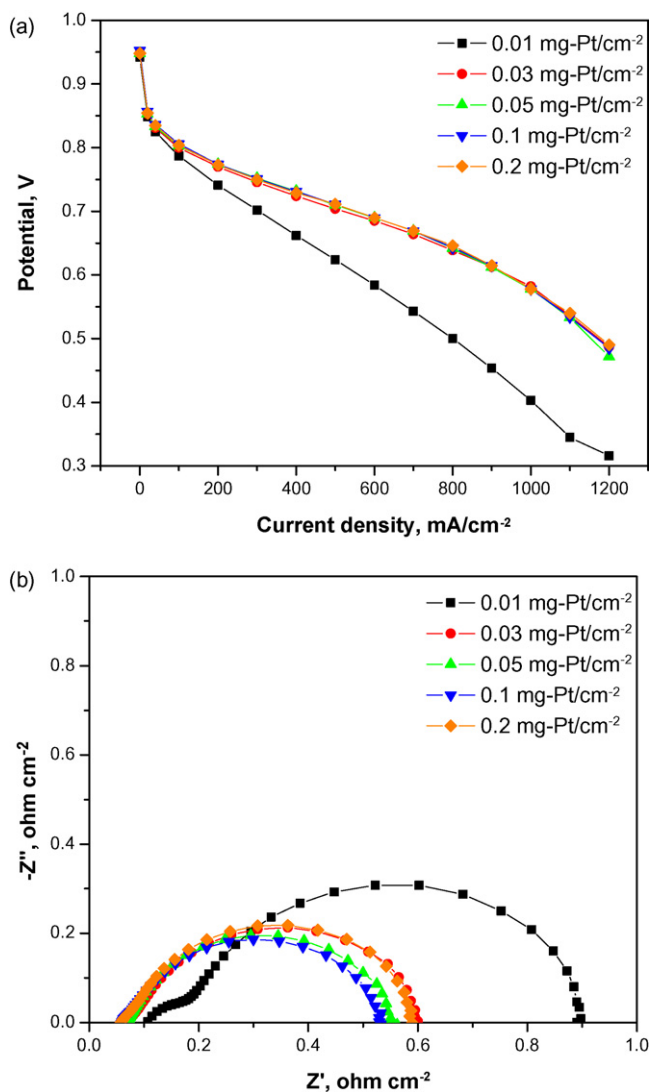


Fig. 1. Effects of anode catalyst loading on (a) cell performance and (b) Nyquist plot. Cathode catalyst loading = 0.4 mg Pt cm⁻².

is below 1 A cm⁻². This difference is negligible and inevitable in laboratory-scale MEA fabrication. On decreasing the catalyst loading from 0.03 to 0.01 mg Pt cm⁻², however, the cell potential decreases significantly in the measured current density region. Impedance spectra presented in Fig. 1(b) show that the ohmic and charge-transfer resistances are almost constant for the single cells with a Pt loading from 0.2 to 0.03 mg Pt cm⁻², namely, 0.06 and 0.47–0.53 Ω cm², respectively. By contrast, a single cell with a Pt loading of 0.01 mg Pt cm⁻² has a different shape of Nyquist plot from the others. The ohmic resistance increases to 0.11 Ω cm² and two arcs are present. This implies that the charge-transfer resistance for the anode reaction is comparable with that for the cathode reaction [17], and results in a reduction in cell performance. Since the cathode was identically prepared for all the single cells, the charge-transfer resistance for the cathode could be assumed to be same at about 0.5 Ω cm², as revealed for the single cells with a Pt loading from 0.2 to 0.03 mg Pt cm⁻². Since the sum of the diameters of the two arcs is calculated to be 0.79 Ω cm² by subtracting the ohmic resis-

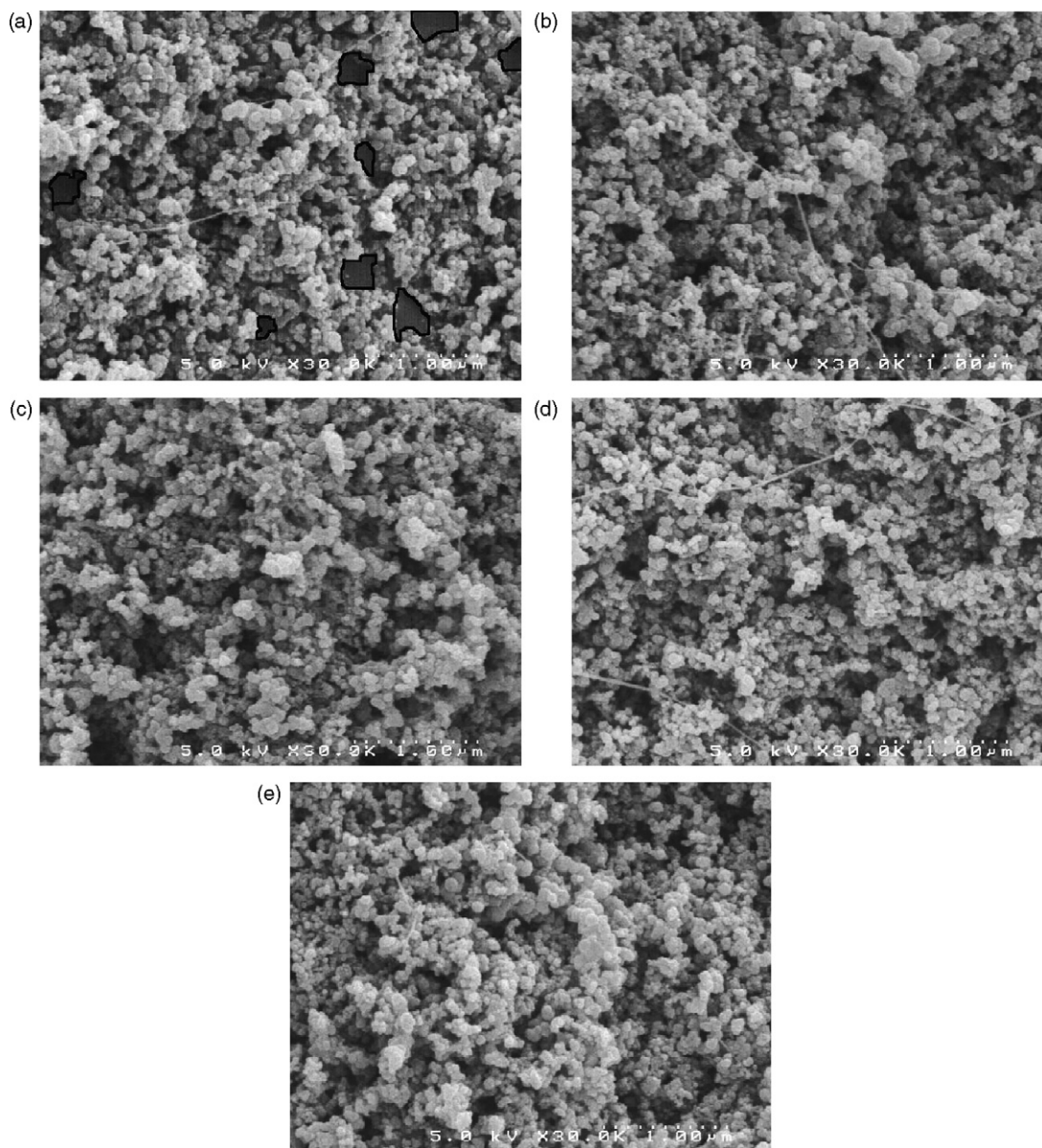


Fig. 2. Scanning electron micrographs of surface morphology of anode catalyst layer: (a) 0.01, (b) 0.03, (c) 0.05, (d) 0.1, and (e) 0.2 mg Pt cm⁻².

tance ($0.11 \Omega \text{ cm}^2$) from the right point of intersection with the x -axis ($0.9 \Omega \text{ cm}^2$), the charge-transfer resistance for the anode reaction is estimated to be $0.29 \Omega \text{ cm}^2$.

The surface morphology of the MEAs was investigated by scanning electron microscopy. As shown in Fig. 2(a), there is a lack of coverage of catalyst particles on the membrane as indicated by thick outlines. On the other hand, this feature is not observed for higher loadings. Thus, the increase in charge-transfer resistance of the anode and the resulting performance loss can be attributed to the isolation of catalyst particles in the anode with a Pt loading of $0.01 \text{ mg Pt cm}^{-2}$. The increase in ohmic resistance could also be caused by the catalyst isolation since the ionomer in the anode catalyst layer would be also disconnected. The effects of anode Pt loading on the performance and resistance of single cell are displayed in Fig. 3. The data suggest that $0.05 \text{ mg Pt cm}^{-2}$ is an optimum Pt loading for the anode.

3.2. Effect of cathode catalyst-gradient loading on fuel cell performance

To examine the effects of cathode catalyst loading on cell performance, i - V curves were measured for the single cells with cathode catalyst loadings from 0.1 to $0.55 \text{ mg Pt cm}^{-2}$ and presented in Fig. 4. In contrast to Fig. 1(a), with increasing catalyst loadings from 0.1 to $0.4 \text{ mg Pt cm}^{-2}$, the cell performance is improved markedly over the measured current density region. For the single cell with a catalyst loading of $0.55 \text{ mg Pt cm}^{-2}$, the voltage dropped abruptly at high current densities. This is probably due to mass-transport resistance caused by the thick electrode layer.

Based on the above results, gradient electrodes were fabricated with an average Pt loading of $0.4 \text{ mg Pt cm}^{-2}$. The distribution of Pt loading for the gradient electrodes is shown in Fig. 5(a). In these electrodes, the catalyst loading increases from

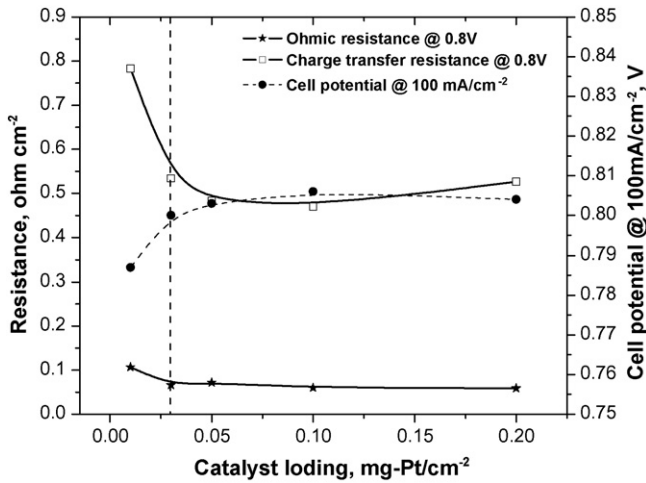


Fig. 3. Effects of anode catalyst loading on ohmic and charge-transfer resistance and cell potential at 100 mA cm⁻². Cathode catalyst loading = 0.4 mg Pt cm⁻².

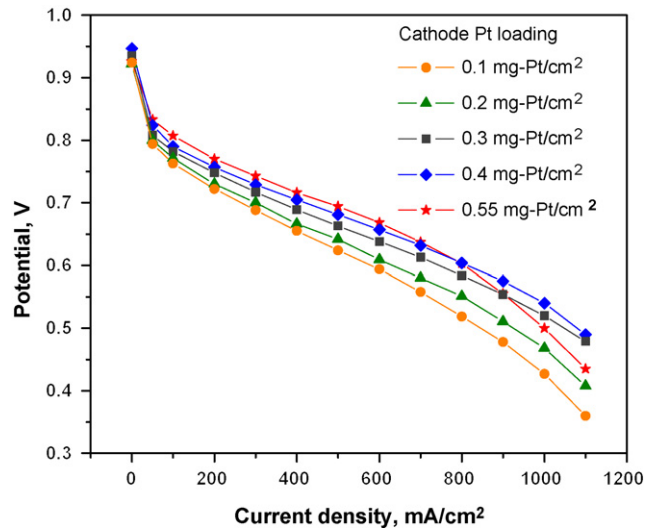


Fig. 4. Effects of cathode catalyst loading on cell performance. Anode catalyst loading = 0.4 mg Pt cm⁻².

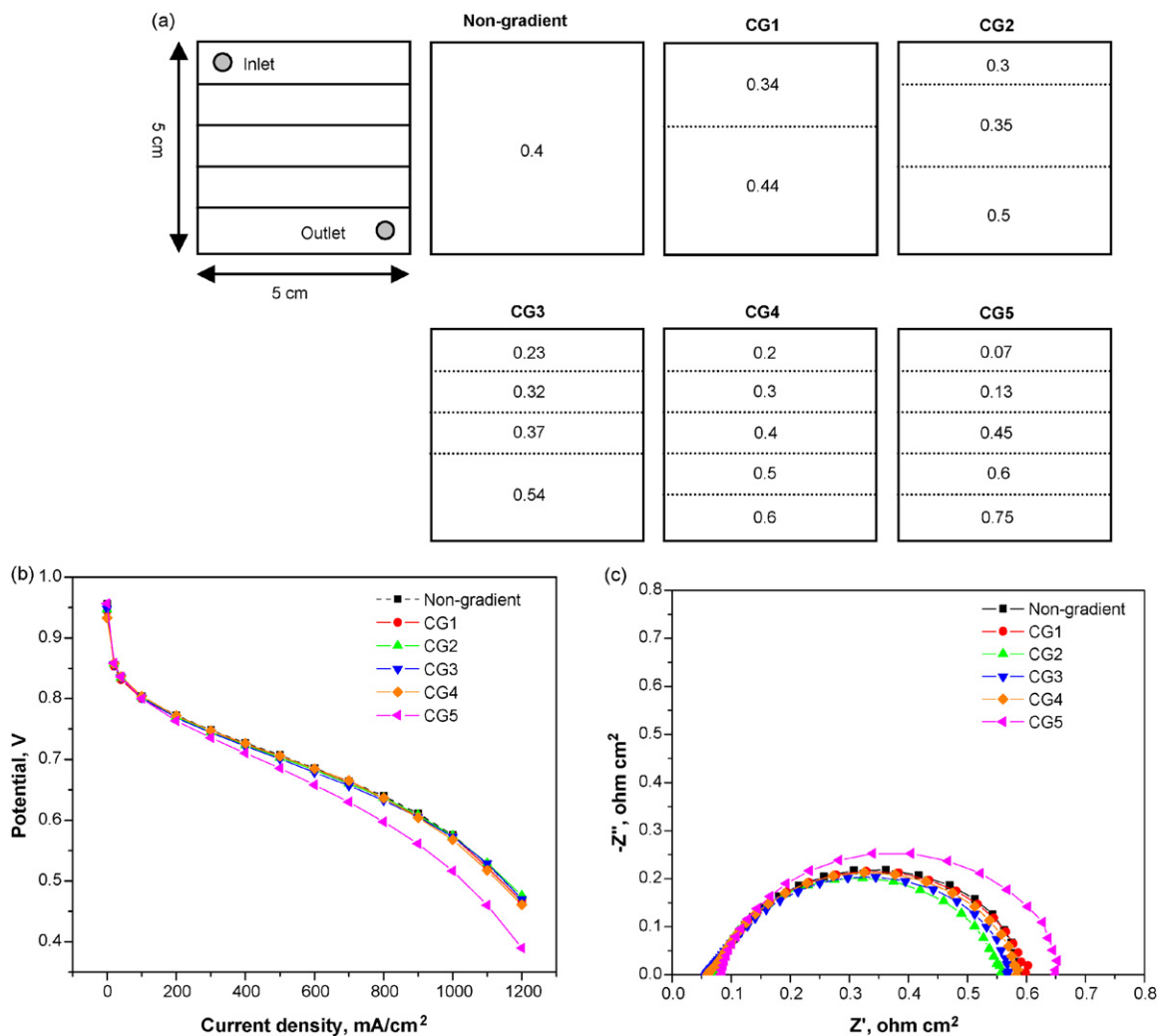


Fig. 5. (a) Distribution of cathode catalyst loading (mg Pt cm⁻²) designed in this study. Average Pt loading for cathode is kept at 0.4 mg Pt cm⁻². (b) Performance and (c) Nyquist plots for single cells fabricated with non-gradient and gradient electrodes described in (a). Anode catalyst loading = 0.2 mg Pt cm⁻².

the inlet to the outlet to counteract the depletion of reactants in the gas stream. For example, catalyst-gradient electrode 1 (CG 1) is composed of two zones, namely, 10 cm² with 0.34 mg Pt cm⁻² and 15 cm² with 0.44 mg Pt cm⁻². In the same manner, CG 2 consisted of three zones: 5 cm² with 0.3 mg Pt cm⁻², 10 cm² with 0.35 mg Pt cm⁻² and 10 cm² with 0.5 mg Pt cm⁻². The distributions are based on the five-channel, semi-serpentine, flow-field geometry of the graphite block used in this study. The average Pt loading is 0.4 mg Pt cm⁻². To eliminate possible loss of cell performance caused by low catalyst loading of anode, this loading is set to 0.2 mg Pt cm⁻². The polarization curves for the single cells with a catalyst-gradient cathode as described in Fig. 5(a) are given in Fig. 5(b). Single cells with catalyst-gradient electrodes CG 1, 2, 3 and 4 exhibit almost the same performance as that with a conventional (non-gradient) electrode. In case of CG 5, a significant decrease in cell performance is observed, which is probably due to the too low

catalyst loading in the inlet region (0.07 mg Pt cm⁻²) and/or to large deviation in the thickness of the catalytic layer. Since the catalyst loading increases by more than 10 times from the inlet to the outlet region, the electrode thickness will also proportionally increase over these regions, resulting in a poor contact between the cathode and backing gas-diffusion media. Impedance spectra for the single cells presented in Fig. 5(b) support the conclusion that higher charge-transfer resistance for the single cell with CG 5 results in a lower cell performance. It should be noted that for the single cells with CG 1, 2, 3 and 4 electrodes, the deviation of thickness in the cathode has little effect on performance. This can be attributed to a much smaller deviation in the cathode thickness that may be compensated by the compression pressure applied in cell assembly.

To investigate in detail the effects of a catalyst-gradient cathode on cell performance, the average catalyst loading was

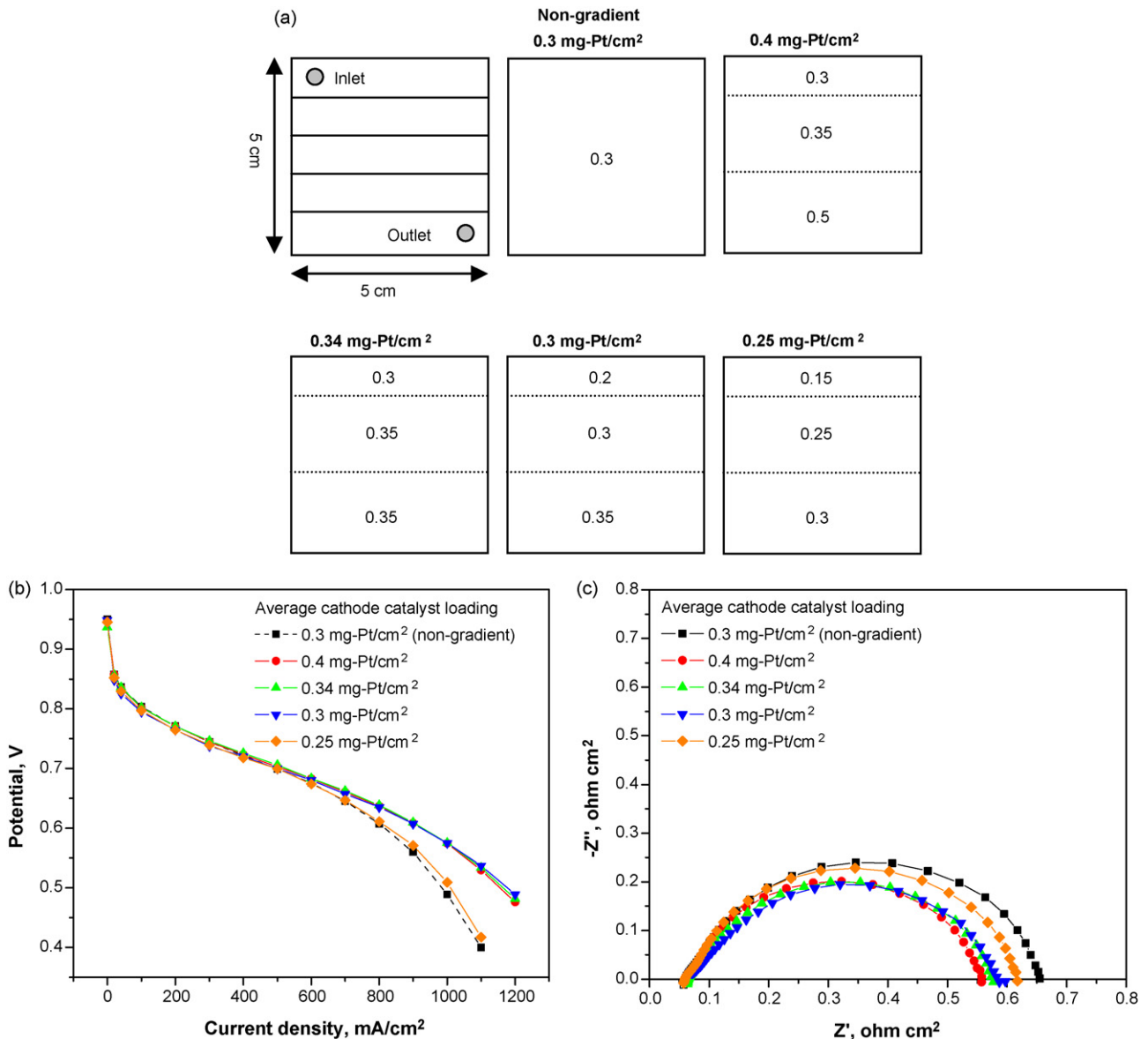


Fig. 6. (a) Distribution of cathode catalyst loading (mg Pt cm⁻²) designed in this study. Average Pt loading for cathode is 0.25, 0.3, 0.34 and 0.4 mg Pt cm⁻². (b) Performance and (c) Nyquist plots for single cells fabricated with non-gradient and gradient electrodes, as described in (a). Anode catalyst loading = 0.2 mg Pt cm⁻².

reduced from 0.4 to 0.34, 0.3 and 0.25 mg Pt cm⁻². The distribution of catalyst loading over the active electrode area is shown in Fig. 6(a), while the cell performance is given in Fig. 6(b). The latter reveals that the non-gradient electrode with a Pt loading of 0.3 mg Pt cm⁻² has almost the same performance as the gradient electrode with average loading of 0.25 mg Pt cm⁻², and that the gradient electrodes with an average loading from 0.4 to 0.3 mg Pt cm⁻² has almost the same performance.

It is remarkable that for the same average loading of 0.3 mg Pt cm⁻², the performance of the catalyst-gradient electrode exhibits higher performance. At a current density of 900 mA cm⁻², the cell voltage is 0.56 and 0.61 V for the non-gradient and the gradient electrode, respectively. The maximum power density is calculated to be 504 and 590 mW cm⁻² for the non-gradient and the gradient electrode, respectively. The enhancement of cell performance by using the catalyst-gradient electrode is magnified at high current densities, which implies that the gradient electrode increases the local reaction rate of the electrode due to higher catalyst loading in the outlet region [18,19]. These results clearly show that by using the catalyst-gradient method, the performance of the fuel cell can be improved while maintaining the same level of Pt usage. Alternatively, by comparing the cell performance of the non-gradient electrode with an average loading of 0.3 mg Pt cm⁻² with that of the gradient electrode with an average loading of 0.25 mg Pt cm⁻², it can be concluded that by using the catalyst-gradient electrode method, the Pt loading can be reduced without performance loss.

4. Conclusions

From studies of single cells with different anode catalyst loading, it is found that the Pt loading can be reduced to as low as 0.03 mg cm⁻² with pure hydrogen. At lower loadings, i.e., 0.01 mg cm⁻², the cell performance is drastically lowered. This is probably due to poor surface coverage of platinum particles on the membrane.

At an average catalyst loading of 0.25 and 0.3 mg cm⁻², the gradient cathodes give better performance than conventional

electrode on account of the presence of more platinum particles at the gas outlet part of the cell where the oxygen concentration is low, particularly at high current densities. The presence of more platinum particles improves the local reaction rate of the electrode at the outlet region. By contrast, a conventional electrode with a uniform catalyst loading gives an inferior performance. Thus, by using the gradient electrode suggested in this study, platinum usage can be reduced.

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