Short communication

Improving the DMFC performance with Ketjen Black EC 300J as the additive in the cathode catalyst layer

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ABSTRACT

Ketjen Black EC 300J with an extremely high mesoporous area and electrical conductivity, was used as an additive in the cathode catalyst layer to improve the DMFC (direct methanol fuel cell) performance. Ketjen Black EC 300J and the catalyst ink were characterized by TEM. The cathode catalyst layers were characterized by SEM, *in situ* cyclic voltammetry and *I–V* curve measurements. Ketjen Black EC 300J additive increased the dispersion extent of Pt black particles and improved the Pt utilization. In addition, the pore size and porosity was increased when Ketjen Black EC 300J was added into the cathode catalyst layer. The cathode catalyst layer with Ketjen Black EC 300J additive showed a greater single cell performance than the cathode catalyst layer without any additive, especially in the air-breathing mode. These results suggested that the performance improvement was attributed to the increased Pt utilization, oxygen diffusion and water removal capability when Ketjen Black EC 300J was added into the cathode catalyst layer.

1. Introduction

In a direct methanol fuel cell (DMFC), water is produced at the cathode by oxygen reduction reaction as well as transported from aqueous anode due to diffusion and electro-osmotic drag [1], and the presence of a large amount of water is prone to flood the cathode, which reduces its performance, especially in an air-fed DMFC [2]. Pt black catalyst is widely used in the cathode of a DMFC because it forms a thin cathode catalyst layer and has a good methanol tolerance [3], however, the Pt black catalyst is hydrophilic and easy to be flooded at a low airflow rate, so the Pt black cathode catalyst layer needs to be urgently optimized.

Much effort has been made to optimize the electrode structure of proton electrolyte membrane fuel cell (PEMFC) and DMFC by using different fabrication methods and pore-forming materials [4–12]. So far, the catalyst-coated membrane structure has been considered to be more beneficial to improve catalyst utilization and mass transport properties of the electrode than other electrode structures [4]. And it is also reported that the pore-forming materials were effective to improve the porosity of the catalyst layer and microporous layer by thermal or acid treatment, however, the pore former increased the resistance due to some unexpected large voids [6], and a trace amount of pore-forming materials may poison the electrode. It is known that highly mesoporous carbon blacks have a good gas diffusion and water handling capability [13], which are promising to be used as a substitute of the pore-forming materials [14,15]. Ketjen Black EC 300J has been used to improve the electrical conductivity of the electrode as an additive in lithium ion battery and alkaline fuel cell [16–18], and it has also been employed as the catalyst support and the material of microporous layer in PEMFC and DMFC due to its high mesoporous area and porosity [19–22]. In view of its favorable electrical conductivity and mesoporous qualities, we have examined the use of Ketjen Black EC 300J as an additive in the Pt black cathode catalyst layer of a DMFC. In this work, as-received Ketjen Black EC 300J was mixed with Pt black catalyst to form the cathode catalyst layer onto the Nafion membrane by the modified decal method, therefore, a more porous cathode catalyst layer was prepared without any additional post-treatment. TEM measurement was used to observe the distribution of Pt black catalyst and Ketjen Black EC 300J in the catalyst ink. SEM measurement was conducted to demonstrate the pore structure and thickness of the cathode catalyst layer. *In situ* cyclic voltammetry (CV) and cell polarization curves were carried out to investigate the improvement of Pt utilization and cell performance, respectively.

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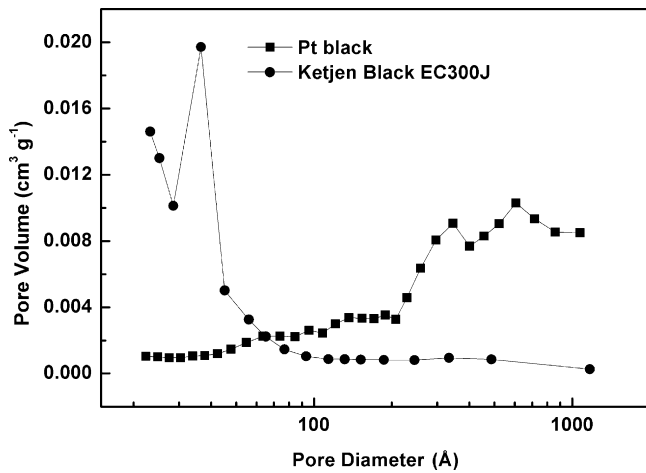E-mail address: gqsun@dicp.ac.cn (G. Sun).

Fig. 1. Pore distribution of Ketjen Black EC 300J and Pt black catalyst.

2. Experimental

2.1. Preparation of membrane and electrode assembly

The anode and cathode catalyst layers were prepared by the modified decal method [23]. To prepare the cathode catalyst layer with carbon black additive, a suitable amount of Pt black catalyst (Johnson Matthey Corp.) and Ketjen Black EC 300J (the optimum weight ratio of Pt black catalyst and Ketjen Black EC 300J was 9:1) was mixed into a water/alcohol solution along with a 5 wt.% Nafion solution (Dupont) and the resulting mixture was ultrasonically agitated with vigorous mechanical stirring to form a homogeneous ink. The ink was then sprayed onto a piece of clean PTFE decal plank. For comparison, a Pt black catalyst layer without carbon black additive was also prepared as described above. The Pt loading in the Pt black cathode catalyst layer with and without Ketjen Black EC 300J additive was 2.4 ± 0.1 mg cm^{-2}, and the optimum Nafion content was 15 wt.% in the cathode catalyst layer with Ketjen Black EC 300J additive (denoted as CCL-1) and 10 wt.% in the cathode
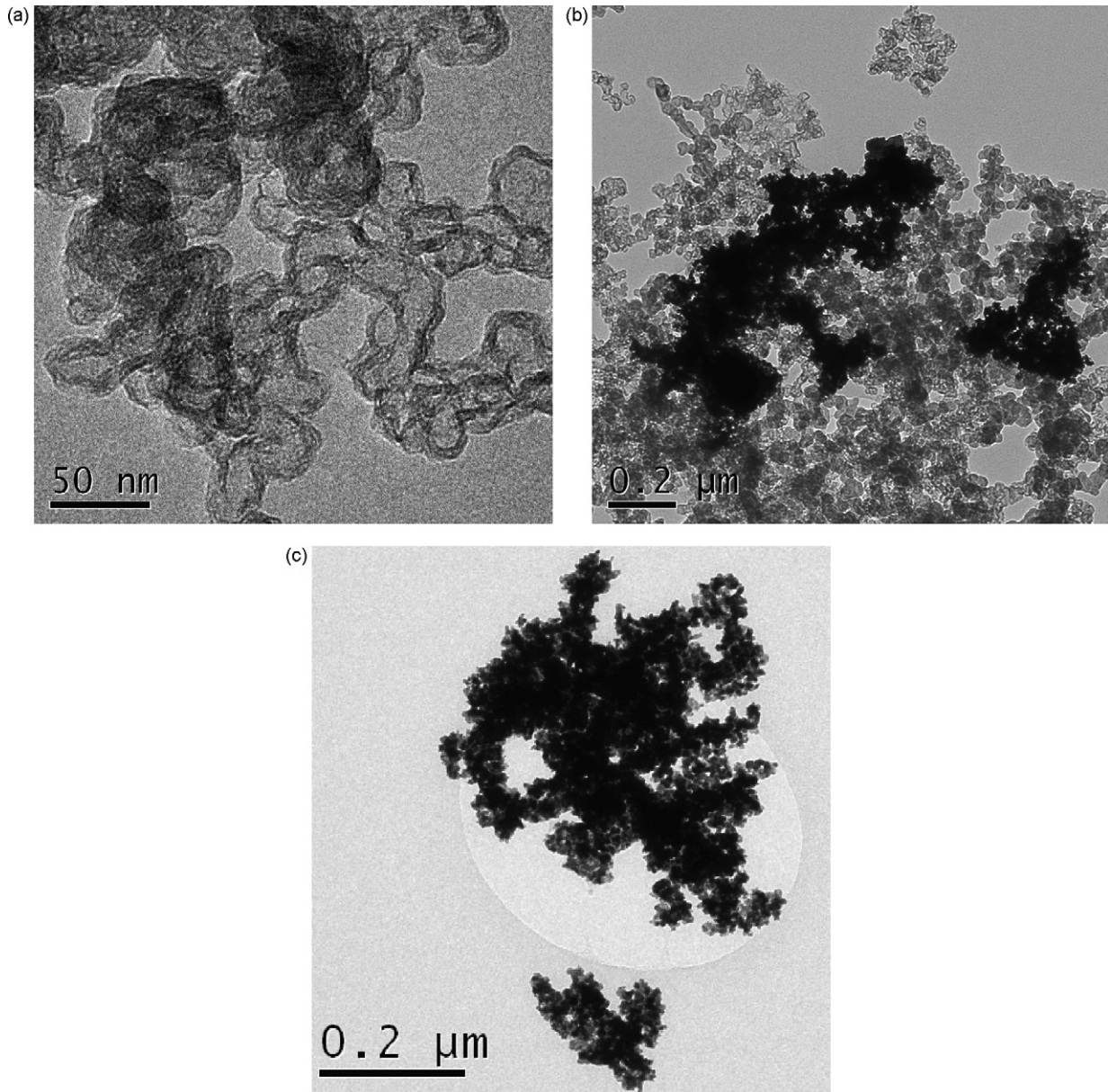

Fig. 2. TEM images of Ketjen Black EC 300J (a) and Pt black catalyst ink with (b) and without Ketjen Black EC 300J additive (c).

catalyst layer without carbon black additive (denoted as CCL-2), respectively. In all cases, the identical anode catalyst layers were prepared by spraying anode ink onto a piece of PTFE decal blank and then drying at room temperature. The resulting PtRu black (Johnson Matthey Corp.) loading was 4.5 mg cm^{-2} and the Nafion content was 15 wt.% in the anode catalyst layer. The anode and cathode decal blanks were placed to two sides of Nafion 115 in the Na$^+$ form and hot-pressed at 190 °C and 30 atm for 3 min. After the decal blank was removed, the prepared catalyst-coated membrane (CCM) was re-protonated to the H$^+$ form of the Nafion membrane in 0.5 M sulfuric acid at 80 °C for at least 1 h, followed by rinsing in deionized water. Finally, anode and cathode diffusion backings (2 cm × 2 cm) were placed onto the corresponding sides of the CCM to form the MEA by hot-pressing at 140 °C and 30 atm for 2 min.

2.2. Single cell test

The single cell test was conducted in active and air-breathing DMFC modes. In the active DMFC mode, the MEA was fitted between two stainless steel plates with a spot-shaped flow field [23]. The polarization curves were obtained using a Fuel Cell Test System (Arbin Instrument Corp.) under the operation conditions of 80 °C, 1 mL min^{-1} of 1.5 M methanol solution and 240 mL min^{-1} of 0.1 MPa non-humidified oxygen/air. In the air-breathing DMFC mode, the cathode plate had a series of 3 mm diameter holes to allow the passage of ambient air, the operation conditions are 60 °C and 0.5 mL min^{-1} of 1 M methanol solution.

2.3. Analysis of Ketjen Black EC 300J, Pt black catalyst and cathode catalyst layer

N$_2$ adsorption of Ketjen Black EC 300J and Pt black catalyst was carried out using an ASAP2010 Micromeritics Instrument at −196 °C. Ketjen Black EC 300J and the catalyst ink were examined

by a Fei Tecnai G^2 spirit microscope. The surface and cross-sectional morphology of the cathode catalyst layers was observed by Philips XL-30 SEM. *In situ* cyclic voltammetry (CV) of the cathode catalyst layers was performed using an EG&G PAR 273 potentiostat at a scan rate of 50 mV s^{-1} as described by Thomas et al. [24].

3. Results and discussion

Fig. 1 shows the pore size distribution of Ketjen Black EC 300J and Pt black catalyst. The particle size of Pt black catalyst was calculated from XRD pattern to be 5.6 nm, however, Pt black particles are prone to conglomerate together and form larger agglomerates [25]. The pore size of Pt black catalyst was mainly distributed in the macropore region, while Ketjen Black EC 300J has a great porosity of mesopore with a mesoporous area of about 560 m^2 g^{-1}, indicating that it has a good gas diffusion and water handling capability [13]. It was also observed from Fig. 1 that Ketjen Black EC 300J exhibited much more mesopore volume than Pt black catalyst, so it is possible to increase the dispersion extent of Pt black catalyst when Ketjen Black EC 300J was added into the Pt black cathode catalyst layer.

Fig. 2(a)–(c) shows the TEM images of Ketjen Black EC 300J, Pt black catalyst ink with and without 10 wt.% Ketjen Black EC 300J additive, respectively. It can be observed that the Ketjen Black EC 300J particles consisted of hollow particles (about 30 nm), which formed long chains entangled together. Ketjen Black EC 300J has a high electrical conductivity due to its high DPH adsorption value of 360 mL 100 g^{-1} [17], so the interconnection will promote that the Ketjen Black EC 300J particles formed a conductive network uniformly. Compared with Fig. 2(b) and (c), it can be concluded that Ketjen Black EC 300J additive was fine to fit in the void among the Pt black particles and thus increased the continuity of electric conductive network.

Fig. 3 shows the surface and cross-sectional SEM images of CCL-1 and CCL-2. It can be seen that the agglomerates are larger in CCL-2
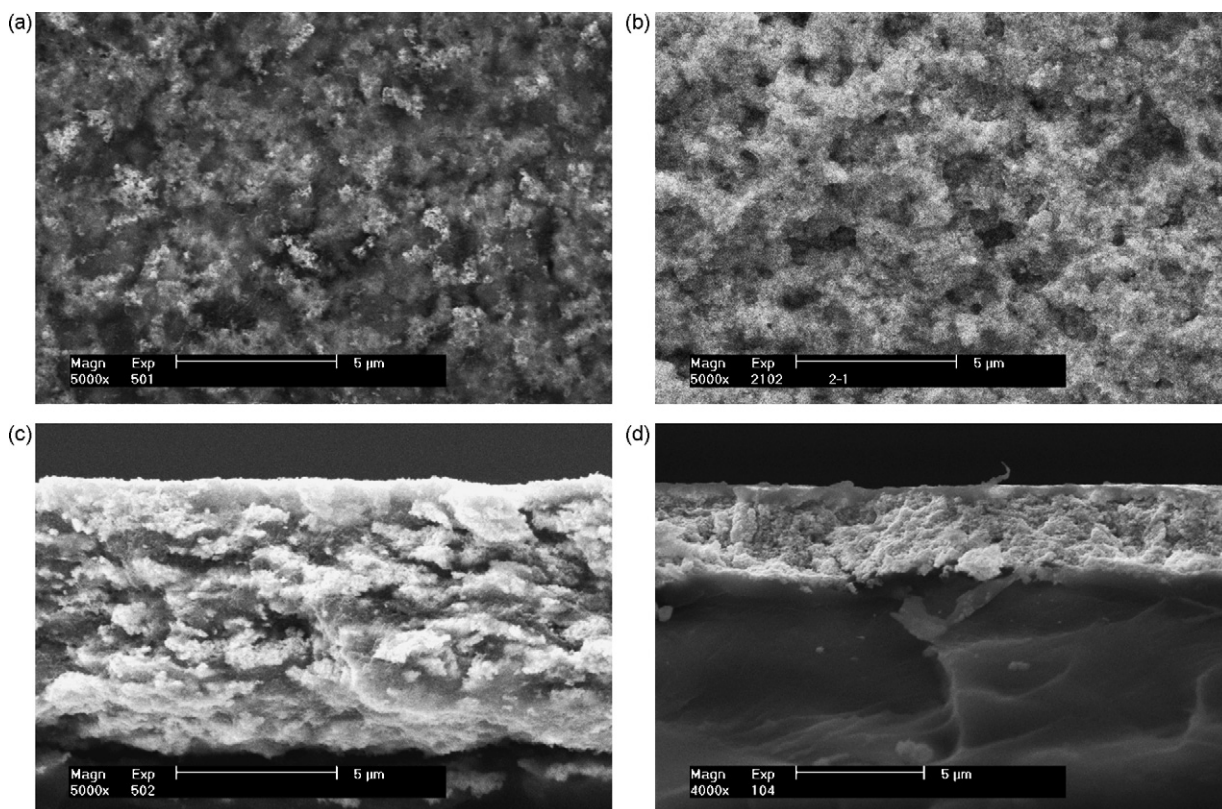

Fig. 3. Surface and cross-sectional SEM images of CCL-1 (a), (c) and CCL-2 (b), (d).

than that in CCL-1, and the Ketjen Black EC 300J additive improved the dispersion extent of the Pt black catalyst in CCL-1, which was corresponding to the result of Fig. 2(b). As shown in Fig. 3(c) and (d), the cross-sectional morphology of CCL-1 is quite different from that of CCL-2. The thickness was increased from 3.8 μm to 9.4 μm due to the Ketjen Black EC 300J additive and a greater Nafion content in CCL-1. It can be also observed that CCL-1 has more and larger pores than CCL-2. The pore size is between 0.44 μm and 0.6 μm in CCL-2, while the pore size is between 1.1 μm and 2.0 μm in CCL-1. According to the result of N_2 adsorption, Ketjen Black EC 300J has a surface area of 829 $m^2\,g^{-1}$ and a pore volume of 1.42 $cm^3\,g^{-1}$, while Pt black catalyst has a surface area of 29.7 $m^2\,g^{-1}$ and a pore volume of 0.13 $cm^3\,g^{-1}$, so the pore structure of the cathode catalyst layer was considered to be greatly changed by Ketjen Black EC 300J additive. It is reported that the pore size distribution of the catalyst layer was largely dictated by the pore size distribution of the powders used to make the catalyst ink [26]. The Ketjen Black EC 300J additive has unmistakably introduced a more open pore structure in the cathode catalyst layer. The increased pore size and amount were expected to promote oxygen transport and support efficient removal of product water to prevent flooding of CCL-1 by providing an open convection path.

Fig. 4 shows *in situ* CVs of the cathode catalyst layers. And the electrochemical active surface (EAS) of CCL-1 and CCL-2 was calculated to be 9.52 $m^2\,g^{-1}$ Pt and 8.14 $m^2\,g^{-1}$ Pt, respectively. When the Nafion content is 10 wt.% in the cathode catalyst layer with 10 wt.% Ketjen Black EC 300J additive, the EAS was 7.12 $m^2\,g^{-1}$, which was smaller than that of CCL-2. Ketjen Black EC 300J additive improved the dispersion extent of the Pt particles and was prone to increase the Pt utilization. However, Ketjen Black EC 300J is more porous and hydrophobic than Pt black catalyst, additional Nafion is required to partially coat the carbon black and form continuous protonic conductive network, so the optimum Nafion content was increased in CCL-1. The result indicated that Ketjen Black EC 300J additive increased the contact area between Pt particle and ionomer in the cathode catalyst layer, thus enhanced the Pt utilization.

Fig. 5 shows the performances of DMFC with CCL-1 and CCL-2 under 80 °C, 240 mL min^{-1} of 0.1 MPa non-humidified oxygen and air, respectively. The current density at cell voltage of 0.4 V was 362 mA cm^{-2} in the CCL-1 cathode and 268 mA cm^{-2} in the CCL-2 cathode, respectively when both cathodes were fed with oxygen, and there was 35.1% increase of current density for the CCL-1 cathode compared with the CCL-2 cathode, which was mainly due to the
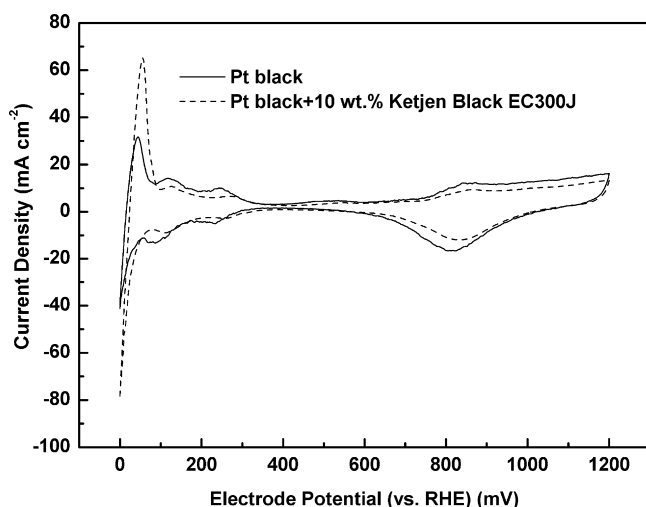

Fig. 5. Curves of cell voltage vs. current density under the conditions of 80 °C, 1 mL min^{-1} of 1.5 M methanol solution and 240 mL min^{-1} of 0.1 MPa non-humidified oxygen/air. Anode: 4.5 mg cm^{-2} PtRu black; cathode: 2.4 ± 0.1 mg cm^{-2} Pt black; membrane: Nafion 115.

Fig. 6. Curves of cell voltage and power density vs. current density under the conditions of 60 °C, 0.5 mL min^{-1} of 1 M methanol solution and air-breathing. Anode: 4.5 mg cm^{-2} PtRu black; cathode: 2.4 ± 0.1 mg cm^{-2} Pt black; membrane: Nafion 115.

improvement of Pt utilization in CCL-1. While in the air-fed DMFC at the identical gas flow rate, there was 84.1% increase of current density at 0.4 V, which was ascribed to the improvement of both oxygen diffusion and water removal capability [23]. Although the thickness of the cathode catalyst layer was greatly enlarged in CCL-1, the oxygen permeability in CCL-1 was greatly enhanced. Interestingly, the difference between the two CCLs increased much larger when the cathode was operated under the air-breathing mode. As shown in Fig. 6, the CCL-2 cathode gave a great performance decline, and there was 3.5 times increase of current density at 0.4 V for the CCL-1 cathode. The maximum power density of DMFC with CCL-1 and CCL-2 was 48.9 mW cm^{-2} and 19.0 mW cm^{-2}, respectively. These results suggested that the CCL-1 cathode was more beneficial for oxygen diffusion and water removal than the CCL-2 cathode, especially at a relatively low airflow rate.

4. Conclusions

Ketjen Black EC 300J with a high mesoporous area and electrical conductivity, was used as the additive to prepare the cathode catalyst layer. TEM image showed that Ketjen Black EC 300J additive improved the dispersion extent of Pt black catalyst and provided

Fig. 4. *In situ* CVs of the cathode catalyst layer with and without Ketjen Black EC300J at 80 °C, recorded at a scan rate of 50 mV s^{-1}. Deionized water was fed to the cathode and humidified H_2 was fed to the anode.
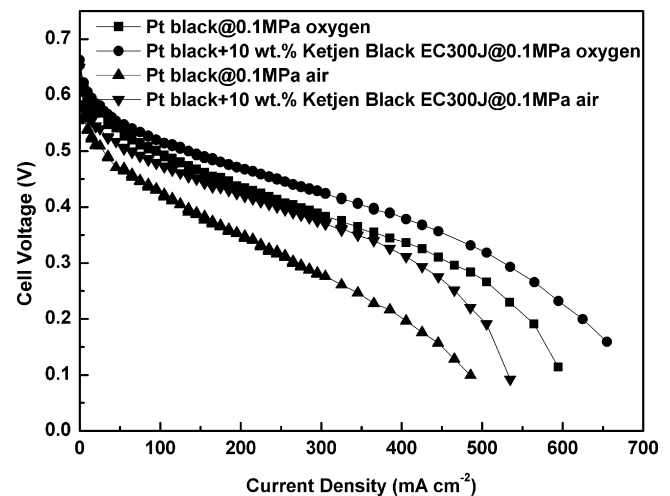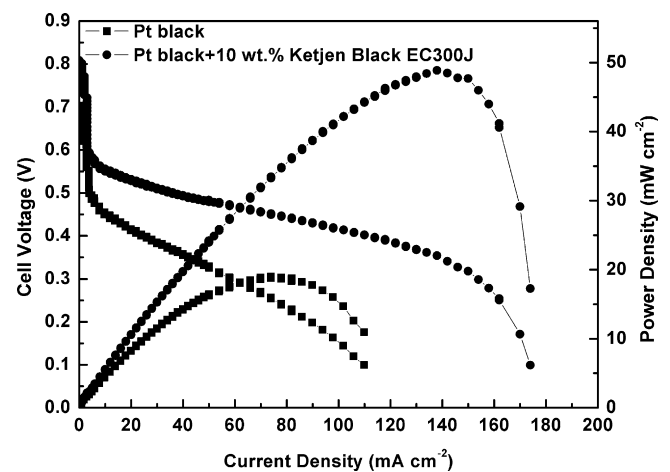
a continuous network in the cathode catalyst layer. *In situ* cyclic voltammetry result verified that the electrochemical surface area was improved from $8.14 \, \text{m}^2 \, \text{g}^{-1}$ Pt to $9.52 \, \text{m}^2 \, \text{g}^{-1}$ Pt in the cathode catalyst layer with Ketjen Black EC 300J additive. In addition, the pore size and porosity were greatly increased in the cathode catalyst layer with Ketjen Black EC 300J additive. The cathode catalyst layer with Ketjen Black EC 300J additive showed a greater single cell performance than the cathode catalyst layer without any additive, especially in the air-breathing mode. The maximum power density of the cathode catalyst layer without and with Ketjen Black EC 300J additive was $19.0 \, \text{mW} \, \text{cm}^{-2}$ and $48.9 \, \text{mW} \, \text{cm}^{-2}$, respectively under $60 \, ^\circ\text{C}$ and air-breathing mode. These results suggested that the performance improvement was ascribed to the increased Pt utilization, oxygen diffusion and water removal capability when Ketjen Black EC 300J was added into the Pt black cathode catalyst layer.

Acknowledgements

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