

Research Article

Highly Durable Direct Methanol Fuel Cell with Double-Layered Catalyst Cathode

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Polymer electrolyte membrane (PEM) is one of the key components in direct methanol fuel cells. However, the PEM usually gets attacked by reactive oxygen species during the operation period, resulting in the loss of membrane integrity and formation of defects. Herein, a double-layered catalyst cathode consisting of Pt/CeO₂-C as inner catalyst and Pt/C as outer catalyst is fabricated to extend the lifetime and minimize the performance loss of DMFC. Although the maximum power density of membrane electrode assembly (MEA) with catalyst cathode is slightly lower than that of the traditional one, its durability is significantly improved. No obvious degradation is evident in the MEA with double-layered catalyst cathode within durability testing. These results indicated that Pt/CeO₂-C as inner cathode catalyst layer greatly improved the stability of MEA. The significant reason for the improved stability of MEA is the ability of CeO₂ to act as free-radical scavengers.

1. Introduction

Direct methanol fuel cell (DMFC) is one of polymer electrolyte membrane fuel cell (PEMFC); it is a promising candidate for electric vehicle and portable electronic devices owing to its high efficiency, environmental friendliness, and convenience [1–5]. Despite an early commercialization of the introduction, the high cost and inferior stability have been main obstacles hindering the widespread commercialization of DMFC technology. One of the key causes for high cost is the use of precious metal catalysts for anode and cathode electrodes to get stable and good fuel cell performance [6]. Moreover, the improvement of stability of fuel cell is a crucial factor on cost. A substantial portion of the published work has been focused on enhancing durable and reliable fuel cell lifetime through electrode structure design, PEM modification, the optimization of operation strategies, and the invention of new electrode materials [7–11]. Unfortunately, DMFCs lifetime has still been short of the 5,000 hours, which will be a challenge of DMFC commercialization [6, 12, 13].

Generally, the voltage degradation of DMFC escalates with the increasing of operation time. One of the main causes of the degradation is the membrane's chemical degradation, which is attributed to reactive oxygen species. Under the condition of transition metal cations, radicals are caused by electrochemical and chemical reactions on DMFC electrode. It can split H₂O₂ generated from two electronic processes of oxygen reduction reaction, or direct reaction of hydrogen and oxygen on cathode [13–16]. These conditions lead to the attack of side chain of perfluorinated sulfonic acid ionomers, resulting in the loss of membrane integrity and formation of defects. The membrane is attacked by free-radicals, which shortens the lifetime of fuel cell. Hence, free-radical should be eliminated to enhance the stability of fuel cell.

CeO₂ ceramic materials are widely used in various application fields, such as catalyst carrier for fuel cell, solid electrolyte for solid oxide fuel cells, and scavenger for free-radical in biological systems [17]. In addition, they exhibit a renewable nature, especially in the acidic condition [18, 19]. These properties are attributed to +3 and +4 oxidation

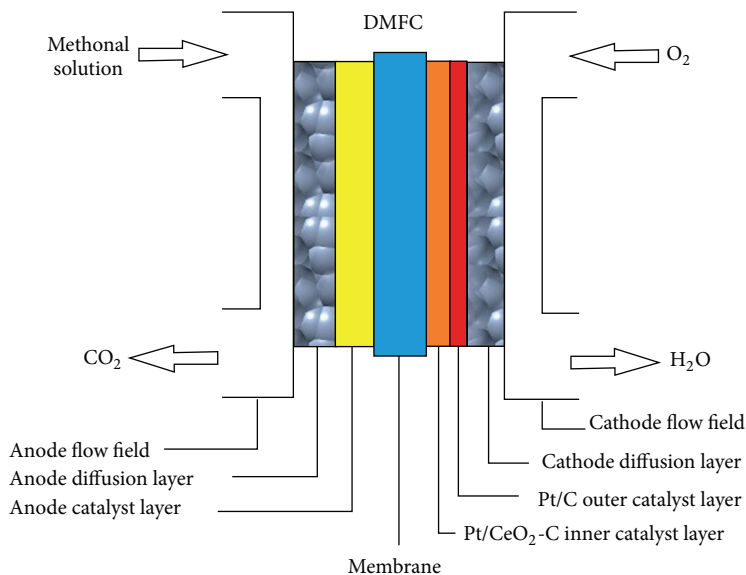


FIGURE 1: The schematic diagram of DMFC.

states of cerium atoms in CeO_2 and the consequent presence of the oxygen storage capacity in CeO_2 [20–22]. In recent years, Nafion/ CeO_2 composite membrane has been prepared to improve the stability of PEM [23–25]. The composite membranes present high durability and a good compatible interface; however, their applications are limited by the sensitivity of temperature and proton conductivity of Nafion membrane [24].

In this work, in order to enhance the stability of DMFC, we design a double-layered catalyst cathode electrode containing Pt/ CeO_2 -C as inner catalyst layer and Pt/C as outer catalyst layer. Our design arises from the free-radical scavenger ability of CeO_2 in fuel cell without effecting proton conductivity of PEM and the convenient preparation. The experimental results show that the membrane electrode assembly (MEA) with double-layered catalyst cathode possesses high durability in comparison with the conventional one.

2. Experimental Detail

2.1. Catalyst Preparation. CeO_2 nanoparticles were synthesized through a precipitation method. Briefly, the dilute $\text{NH}_3\text{-H}_2\text{O}$ solution was dropped into the $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ aqueous solution with magnetic stirring and its pH value reached 10 at 80°C . Then, light yellow suspended solution was aged for 4 h. The product was washed for several times with heated deionized water (Millipore, $18.2\text{ M}\Omega\text{ cm}$) and dried at 80°C for 12 h. The power was calcined at 450°C for 1 h under air.

All homemade catalysts were prepared through the microwave-assisted polyol process (MAPP) as reported by our team [26, 27], and their the metal loading was 40 wt.%. The CeO_2 content of CeO_2 -C was 30 wt.%. In detail, a certain amount of Vulcan XC-72 carbon black (Cabot) was dispersed into 50 mL mixture of isopropyl alcohol and ethylene glycol

(EG) ($v:v = 1:4$) and under ultrasonic treatment for 30 min to form uniform suspension. Then, a calculated amount 0.0385 mol L^{-1} H_2PtCl_6 -EG solution was dropped into the suspension with urgent agitation for 3 h. The pH value of the suspension was adjusted to 12 by using a 1 mol L^{-1} NaOH-EG solution, and the suspension was placed in a microwave oven (Galanz Ltd., 800 W) for consecutive heating for 55 s under flowing Ar. Then, the solution was cooled to room temperature. The pH value of the solution was adjusted to 3 by dropping HNO_3 aqueous solution, which was stirred for 12 h. Finally, the product was washed repeatedly with 80°C deionized water. The homemade Pt/C catalyst was dried at 80°C for 5 h in a vacuum oven. Pt/ CeO_2 -C catalyst and PtRu/C catalyst synthetic process was similar to the above Pt/C preparation.

2.2. MEA Fabrication. All MEAs were fabricated by method as previously reported our team [28]. Geometric area of the MEAs was 5 cm^2 . Homemade PtRu/C catalyst was used as anode catalyst, and the metal loading was 2.5 mg cm^{-2} . The schematic diagram of DMFC with double-layered catalyst cathode was shown in Figure 1. The catalyst layer is made up of the inner layer and the outer layer. Homemade Pt/C was used as cathode outer layer with metal loading of 2 mg cm^{-2} , and the homemade Pt/ CeO_2 -C was used as cathode inner layer with metal loading of 0.5 mg cm^{-2} . The uniform catalyst ink was made from the mixture of the catalyst, 5 wt.% Nafion ionomer solution (DuPont), water, and isopropyl alcohol, and stirred in an ultrasonic bath continuously at 25°C . The Nafion content was 20 wt.%. Then, the catalyst ink was brushed onto the gas diffusion layer which was previously prepared by applying microporous layer to the teflonized carbon paper (Toray paper TGPH 090) [29]. Nafion 117 membrane (DuPont) was used as the solid electrolyte. Prior to MEAs fabrication, the pretreatment of Nafion 117 was

accomplished and treated in 3 wt.% H_2O_2 solution, distilled water, 0.5 mol L^{-1} H_2SO_4 solution, and then distilled water again, at 80°C for 1 h each step. MEAs were fabricated by hot-pressing anode electrode and cathode electrode on either side of Nafion 117 membrane at 135°C , 100 kg cm^{-2} for 90 s. The preparation of conventional MEA was similar to the MEA with cathode double catalyst layers.

2.3. Electrochemical and Characterization Techniques. MEAs were placed in a serpentine flow fields between two graphite plates. Methanol solution (1.5 mol L^{-1}) was supplied to anode at flow rates of 3 mL min^{-1} , and nonhumidified O_2 (ambient pressure) was supplied to cathode at flow rates of 200 mL min^{-1} . DMFCs were operated at 80°C . The single cell performance tests were performed by fuel cell system (Scribner Associates Inc., Series 890e). The polarization and power density curves of MEA were recorded by measuring the current density with voltage gradual reduction from the open circuit voltage to 0.1 V at an interval scale of 10 mV . At each cell voltage, the current density was measured after keeping 3 min in order to the cell approaching steady-state. The potential-time curves were measured in a constant current mode with current density of 150 mA cm^{-2} for 20 h. Electrochemical impedance spectra (EIS) and linear sweep voltammetry (LSV) were carried out by using a CHI 650E electrochemical analysis to investigate the cell performance at 25°C . EIS of the MEAs were carried out at 400 mV with amplitude of 5 mV and the frequency from 0.01 to 10 kHz . LSV was performed to analyze the quantity of permeated methanol. The cathode and the anode were served as working electrode (WE) and a dynamic hydrogen electrode (DHE), respectively. Methanol solution and humidified nitrogen gas were supplied to anode and cathode side, respectively. Meanwhile, the positive potential was applied to WE from 0.2 to 0.9 V (versus DHE) with a scan rate of 1 mV s^{-1} .

X-ray diffraction (XRD) pattern of the catalyst was obtained with a D/max-rB (Japan) diffractometer using a $\text{Cu K}\alpha$ X-ray source, at a scan rate of 4° min^{-1} , with scanning range of 10° to 90° . Morphology and particle size of the catalyst were performed on transmission electron microscopy (TEM, Japan JEOLJEM-2010EX) with an acceleration voltage of 300 kV .

3. Results and Discussion

The structure and morphology of the as-prepared CeO_2 and $\text{Pt/CeO}_2\text{-C}$ hybrids are investigated by means of XRD, TEM, and high-resolution TEM (HRTEM) as shown in Figure 2. XRD patterns of both catalysts show the characteristic (111), (200), (220), and (311) reflections of face centered cubic crystalline Pt and the characteristic (111), (200), (220), (311), (331), and (420) peaks of the cubic fluorite CeO_2 (Figure 2(a)). TEM images reveal that the as-synthesized CeO_2 possesses a highly dispersed square shape with an average size of about 10 nm (Figure 2(b)). In Figure 2(c), the crystal plane distances of 0.31 nm obtained for the CeO_2 (111) plane agree very well with the known crystal plane distance, which further confirms the formation of the

cubic fluorite structured CeO_2 . Figures 3(a)–3(d) are TEM images and particle size distribution histogram of $\text{Pt/CeO}_2\text{-C}$ catalyst and Pt/C catalyst, respectively. The average crystal sizes of Pt particles for $\text{Pt/CeO}_2\text{-C}$ catalyst and Pt/C catalyst are about 2.3 and 2.6 nm , respectively. Pt nanoparticles are uniformly dispersed on CeO_2 , indicating that CeO_2 can promote the particles dispersion.

Since the MEA with double-layered catalyst cathode has high CeO_2 loading on the cathode, the performance is influenced easily by the electrical conductivity and methanol crossover because the $\text{Pt/CeO}_2\text{-C}$ inner cathode catalyst layer with high CeO_2 loading was able to increase charge transfer resistance and the effect of mixed potential. Before the durability investigation of the MEA with double-layered catalyst cathode, the polarization and power density curves of two MEAs are illustrated in Figure 4(a). The MEA with double-layered catalyst cathode shows a slightly lower performance in comparison with conventional MEA. The polarization curve reveals that the open circuit voltage of the MEA with double-layered catalyst cathode decreases from 0.667 to 0.653 V , and the power density curve shows that the maximum power density is degraded from 118.2 to 86.9 mW cm^{-2} . These results can be attributed to the negative shift of onset potential for methanol electrooxidation on $\text{Pt/CeO}_2\text{-C}$ inner catalyst layer and the relatively low electrical conductivity of CeO_2 . Therefore, the effect of mixed potential is increased and open circuit voltage of DMFC is degraded. Additionally, the addition of $30 \text{ wt.}\%$ of CeO_2 to catalyst support increases the catalyst layer's resistance a little bit. Thus, the maximum power density of DMFC with double-layered catalyst cathode is slightly lower than that of the conventional MEA.

The methanol electrooxidation currents of MEA with double-layered catalyst cathode and conventional one are carried out by LSV to estimate the resistance of the cathode for permeated methanol, and the LSV curves are shown in Figure 4(b). At low cathode potential region, the onset potential for methanol electrooxidation at $\text{Pt/CeO}_2\text{-C}$ inner cathode catalyst layer is more negative in comparison with single Pt/C cathode catalyst layer. At high cathode potential region, methanol electrooxidation reaction is not restricted by the catalytic activity of the electrode, but dominated by methanol permeation rate. The limiting current density of double-layered catalyst cathode is about 67.66 mA cm^{-2} , which exhibits relatively higher in comparison with the conventional cathode (around 60.9 mA cm^{-2}). The results reveal that the addition of $\text{Pt/CeO}_2\text{-C}$ to inner cathode catalyst layer increases the mixed potential at cathode and degrades DMFC power slightly.

To find out the effect of $\text{Pt/CeO}_2\text{-C}$ inner cathode catalyst layer more exactly on DMFC performance, EIS of the MEAs with double-layered catalyst cathode and the conventional one are measured at 25°C and DMFC voltage is set at 400 mV . Nyquist diagrams and equivalent circuit diagram of MEAs are listed in Figure 4(c). At the whole frequency, the first arc and second arc are ascribed to the charge transfer resistance and diffusion resistance, respectively. At lower frequency, the inductive loop of the fourth quadrant should be the so-called "pseudoinductive" behavior owing to a higher CO poisoning

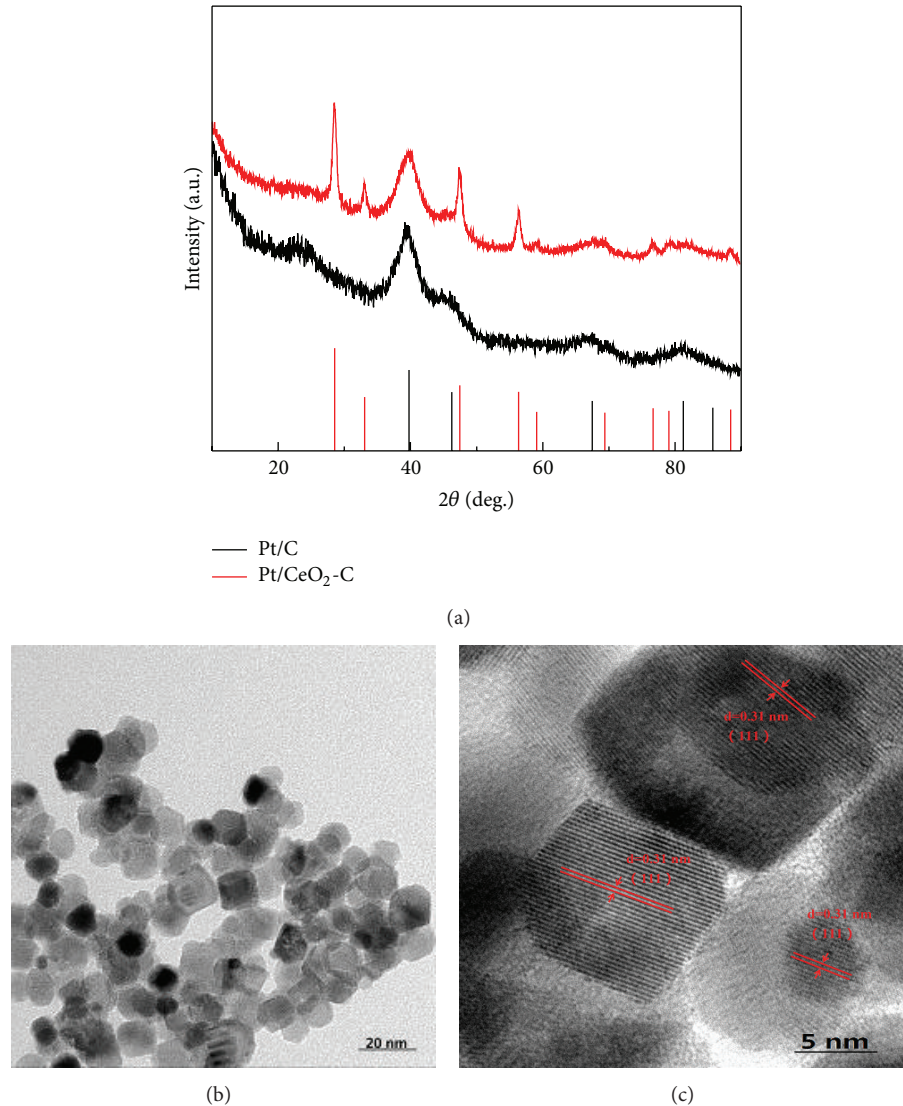


FIGURE 2: (a) XRD patterns of Pt/C catalyst (black line) and Pt/CeO₂-C catalyst (red line); (b) TEM image for CeO₂ particles; (c) HRTEM image for CeO₂ particles.

[29, 30]. According to the related value for the different common elements composing obtained by fitting the EIS data, the R_{Cct} for MEA with double-layered catalyst cathode and conventional MEA is 0.68Ω and 0.55Ω , respectively. The value of Warburg coefficient for MEA with double-layered catalyst cathode ($28.9 \text{ S s}^{0.5}$) is lower than that of conventional MEA ($30.7 \text{ S s}^{0.5}$). The resistance values of other common elements are similar for both MEAs. The results for equivalent circuit fitting EIS indicate that the MEA with double-layered catalyst cathode exhibits slightly higher charge transfer resistance and diffusion resistance than the conventional MEA without any changes in ohmic resistance. This means that the electrochemical reaction of the MEA with double-layered catalyst cathode is slower than that of the conventional one and its mass transfer resistance is relatively higher. EIS results agree well with those of the polarization curves.

Durability behavior was performed in constant current density of 150 mA cm^{-2} for 20 h in order to compare the stability of MEAs with double-layered catalyst cathode and the conventional one. The voltage-time curves are shown in Figure 5. The MEA with double-layered catalyst cathode shows significant improvement over the stability of conventional MEA. The degradation rate for MEA with double-layered catalyst cathode and the conventional cathode is 0.83 and 1.8 mV h^{-1} , respectively. The improvement of MEA stability can be ascribed to the scavenging of free-radicals which would have chemically attacked the membrane and compromised its durability. During the process of free-radical scavenging, the reaction between surface Ce^{3+} and free-radical, its equation is listed by the following reaction [20, 31]:



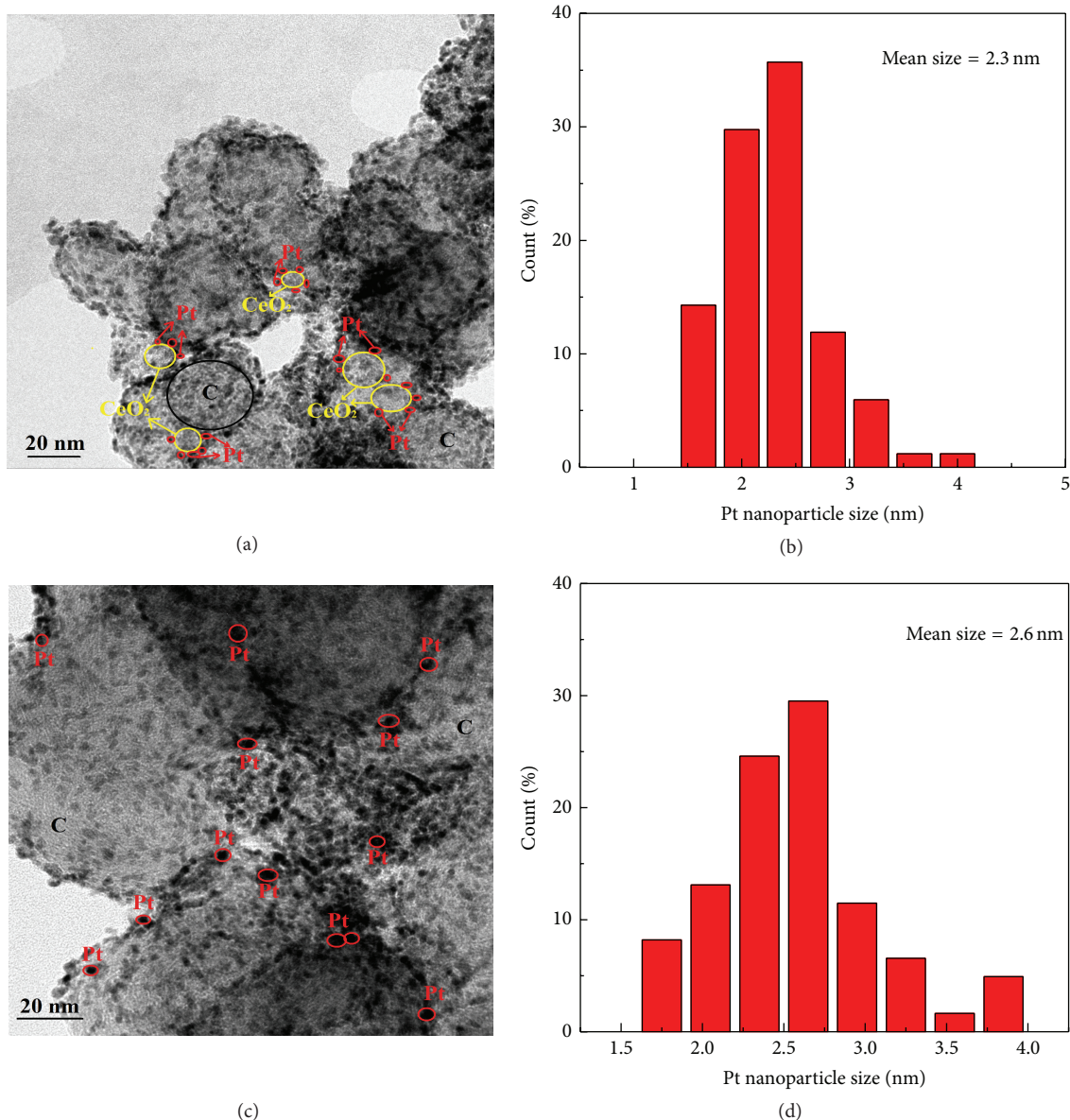
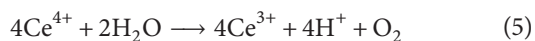
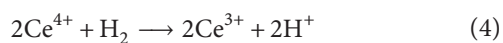
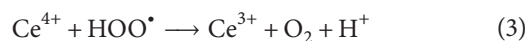
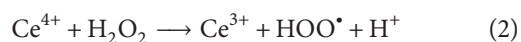


FIGURE 3: (a) TEM image for Pt nanoparticles in Pt/CeO₂-C catalyst and (b) Pt/C catalyst. (c) Particle size distribution histogram of Pt/CeO₂-C catalyst and (d) Pt/C catalyst.

In CeO₂ regeneration process, surface Ce⁴⁺ is reduced back to Ce³⁺ on CeO₂ surface as follows:



The continuous reaction between multivalent cerium ion and free-radical, especially in acidic conditions, improves regenerative nature of CeO₂. Therefore, CeO₂ can continually

react with free-radicals to protect Nafion from attack, resulting in improved durability of MEA.

4. Conclusions

In this study, a double-layered catalyst cathode electrode, consisting of Pt/CeO₂-C as inner catalyst and Pt/C as outer catalyst, was developed to extend the lifetime and minimize the performance loss of the MEA. The maximum power density of MEA with double-layered catalyst cathode was 87.9 mW cm⁻², which exhibited slightly lower than that of the conventional one (117.4 mW cm⁻²). MEA with double-layered catalyst cathode exhibited a low degradation rate of

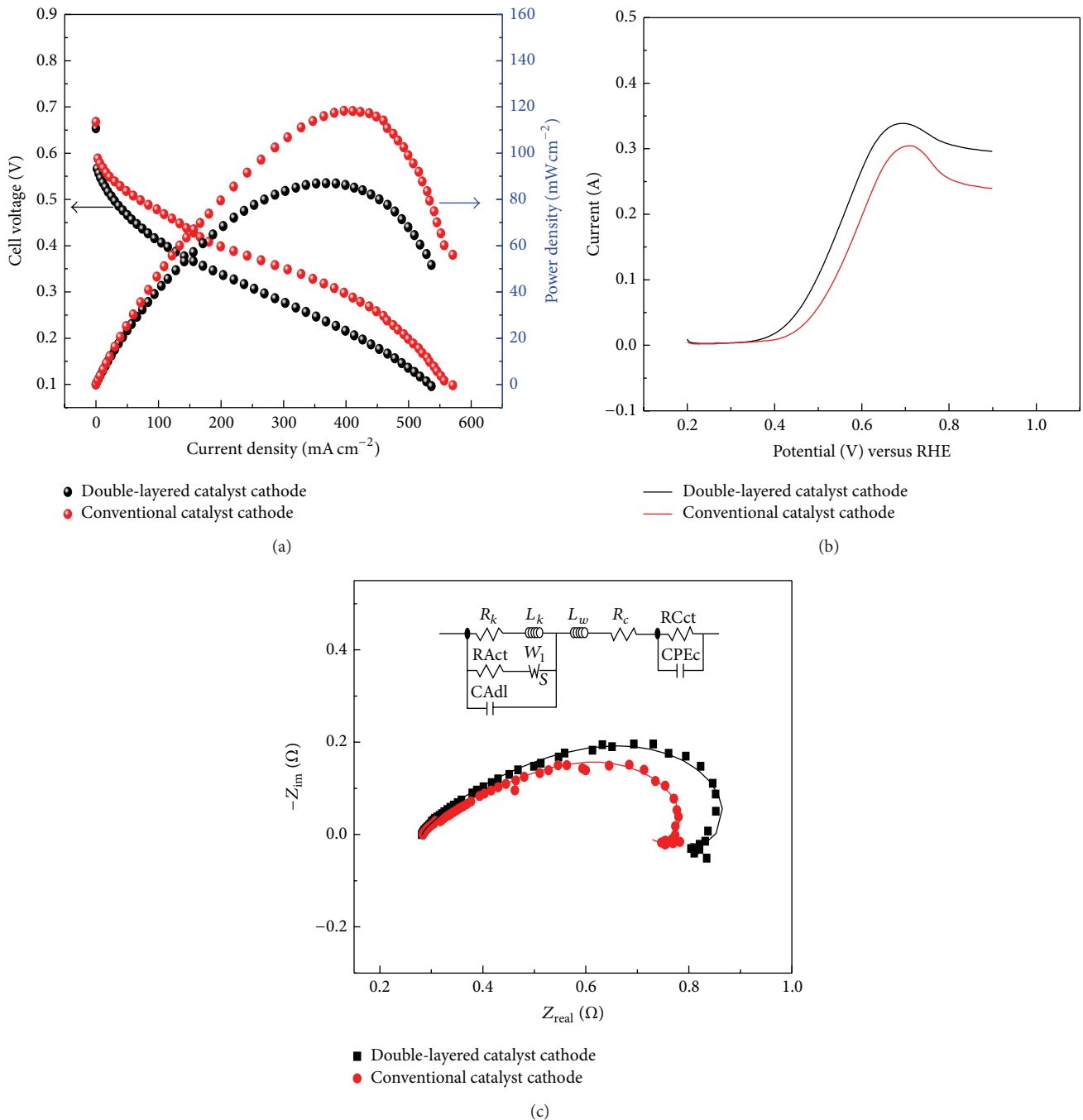


FIGURE 4: (a) Performance of MEA with double-layered and conventional catalyst cathode. Temperature: 80°C . Anode feed: $2 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ solution. Flow rate: 3.0 mL min^{-1} . Cathode feed: oxygen at ambient pressure. Flow rate: 200 mL min^{-1} . (b) Linear sweep voltammograms of methanol permeating through the membranes at the double-layered catalyst and the conventional cathode. (c) Nyquist diagrams of MEA with double-layered catalyst and the conventional cathode at 400 mV ; the lines correspond to the fit by the equivalent circuit. Anode feed: $2 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$ solution. Flow rate: 3.0 mL min^{-1} . Cathode feed: oxygen at ambient pressure. Flow rate: 200 mL min^{-1} .

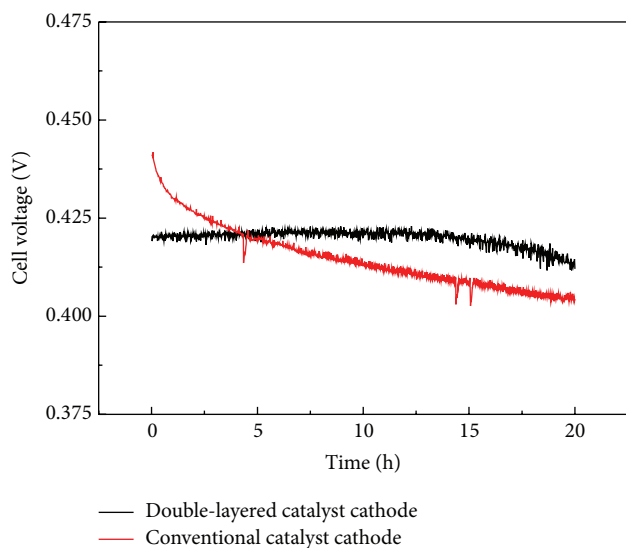


FIGURE 5: Voltage-time curves of the MEA with double-layered and conventional catalyst cathode continuously operated for 20 h at a constant current density of 150 mA cm^{-2} .

0.83 mV h^{-1} , which was around 55% lower than the conventional MEA. Pt/CeO₂-C as free-radical scavengers into inner cathode catalyst layer greatly improved the stability of MEA, although they slightly increased the effect of mixed potential. The improvement of stability can be attributed to the ability of CeO₂ to act as free-radical scavengers.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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