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Preparation of highly active 40 wt.% Pt/C cathode electrocatalysts for DMFC via different routes

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Abstract

A series of 40 wt.% Pt/C electrocatalysts were prepared by a modified polyol process and an improved aqueous impregnation method with different impregnation time. The characterization results of TEM and XRD identically reveal that the size and distribution of Pt nanoparticles on carbon are controllable by modifying impregnation time in both routes. High dispersion of Pt nanoparticles on carbon is achieved by both methods with 15 min impregnation, while aggregation of Pt nanoparticles takes place with prolonging the impregnation time to 36 h, especially in the aqueous impregnation procedure. UV–vis spectroscopy measurements verified that the redox reaction between $PtCl_6{}^{2-}$ and formaldehyde could take place at a slow rate under ambient conditions via a two-step reaction path, where $PtCl_4{}^{2-}$ serves as an intermediate. On the other hand, $PtCl_6{}^{2-}$ anion can be directly reduced to Pt^0 above 333 K in the modified polyol process through an autocatalytic pathway. The short-time-impregnated 40 wt.% Pt/C as cathode electrocatalysts in direct methanol fuel cell performs better than that of long-time-impregnated electrocatalysts. Experimental evidence provides clues for fundamental understanding of elementary steps of the redox reactions, which helps guiding the design and preparation of highly dispersed Pt catalyst with high metal loadings for fuel cells.

Keywords: Pt/C cathode electrocatalysts; DMFC; Polyol process; Aqueous impregnation method

1. Introduction

Highly dispersed Pt/C catalyst with high metal loading is known to be an efficient electrocatalyst for the oxygen reduction reaction (ORR) in direct methanol fuel cells (DMFCs) [1,2]. It can supply more active sites with less volume, i.e., thinner electrode layer. Thus, higher performance can be achieved due to relatively low mass transport loss. However, Synthesis of highly dispersed supported platinum with uniform nanoparticle size still remains a challenge, especially for high metal loading. Great efforts have been made to explore improved synthetic routes by many investigators [3–7]. However, most of previous preparation methods are too complicated to satisfy the requirement of mass production. By far the most attractive synthesis route is still the impregnation process due to its simplicity. However, this route is also limited by its drawbacks of the large average metal particle size, the broad size distribution and the poor reproducibility [8,9]. In this paper, highly active 40 wt.% Pt/C electrocatalysts with Pt particles in the 1–5 nm range were prepared by two different impregnation routes—the modified polyol process and the improved aqueous impregnation method [10]. In both methods, the influence of impregnation time on the dispersion of Pt was comparatively investigated. The steps of preparation were traced by spectroscopic methods, which provide evidence for understanding of the elementary step of redox reaction. This provides the clues for optimizing the operating parameters and helps to avoid painstaking and time-consuming orthogonality experiments.

2. Experimental

XC-72R carbon black (Cabot Corp., $S_{BET} = 236.8\ m^2/g$) was used as support for all of samples. For the impregnation method, formaldehyde was employed as reducing agent. 1 g of XC-72R carbon powder was first suspended in the aque-

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ous solution of appropriate amount of chloroplatinic acid. Then the 5.2 ml of 37% formaldehyde with a mole ratio of $HCHO:PtCl_6^{2-} = 20:1$ was added into the ink. Thereafter, a 0.5 mol/L NaOH solution was gradually added to the suspended mixture until the pH of the mixed solution reached 14. Prior to heating, the mixture was impregnated for 15 min and 36 h under vigorous stirring for two different 40 wt.% Pt/C samples, denoted as HCHO-S (S means short impregnation time) and HCHO-L (L means long impregnation time), respectively. Then, the mixture was refluxed in an oil bath from room temperature to 363 K at a rate of 10 K/min and maintained for 3 h. Finally, strong electrolyte such as $NaNO_3$, NaCl or HCl aqueous solutions was added as sedimentation promoter. The resulting solid was washed with copious distilled water until Cl^- anion was not detected in filtrate by $AgNO_3$ solution, and then dried at 373 K for 10 h in vacuum. For the modified polyol process, ethylene glycol (EG) was used as reducing agent. The process has been described elsewhere [11]. Similarly, two 40 wt.% Pt/C samples with different impregnation time, i.e., 15 min and 36 h were obtained and denoted as EG-S and EG-L, respectively. The atomic absorption spectroscopy (AAS) analysis of filtrate showed that platinum was exclusively deposited on the carbon in both methods.

Specimens were prepared for TEM analysis by ultrasonically suspending the catalyst powder in ethanol. A drop of the suspension was then applied onto clean holy copper grids and dried in air. Samples were examined using the JEOL JEM-2011 electron microscope operated at 100 kV. More than 300 particles were calculated to get the integrated information about the overall distribution of every Pt-based catalyst samples.

X-ray diffraction (XRD) measurements were carried out on a Regaku X-3000 X-ray diffractometer using Cu Kα in radiation with a Ni filter. The tube voltage was maintained at 40 kV, and tube current at 100 mA. The 2 s angular region from 20° to 85° was explored at a scan rate of 5° per min.

UV–vis spectrophotometry was applied to trace the redox on a JASCO Model V-550 recording spectrophotometer. Corresponding to the time of above preparation process, the reaction media was kept agitated for 15 min and 36 h, respectively, and then the mixture was separated by filtration in the aqueous impregnation method. The filtrates were collected and their UV–vis absorption spectra were recorded. In the polyol process, UV–vis spectrophotometry was employed to monitor the reaction solution system without carbon black.

The electrochemical performance tests of the as-prepared 40 wt.% Pt/C as cathode electrocatalysts were carried out under the same operation conditions. The preparation of membrane electrode assemblies (MEAs) and operation conditions of single fuel cell have been described elsewhere [12]. In brief, the anode contained the commercial 20 wt.% Pt-10 wt.% Ru/C catalysts (Johnson Matthey Inc.) with a metal loading of 2 mg/cm^2 and the cathode contained 40 wt.% Pt/C catalyst with a Pt loading of 1.0 mg/cm^2. Nafion®-115 membrane was used as solid electrolyte. Then, the sandwich of anode–membrane–cathode was assembled by hot-pressing. The single cell with an active area of 9 cm^2 was fed with a methanol aqueous solution of 1.0 M in anode and dry oxygen of 0.2 MPa pressure in cathode.

3. Results and discussion

Fig. 1 shows the TEM images of the 40 wt.% Pt/C samples. As observed from Fig. 1(a) and (b), the spherical platinum particles on carbon in EG-S and HCHO-S samples are uniform and well distributed. Based on the measurements of 300 particles in random regions, the average particle size was estimated to be 2.9 nm for EG-S and 2.6 nm for HCHO-S, respectively. The corresponding histogram (Fig. 1(a) and (b)) reveals that the particle size distribution is rather narrow and exhibits the features of a log-normal distribution. When impregnation time was prolonged to 36 h, the average diameter of Pt particles slightly increases from 2.9 to 3.2 nm with the impregnation time increasing to 36 h in the modified polyol process. The distribution curve in Fig. 1(c) indicates that the majority of Pt particles are still mostly concentrated at the smaller particle diameters, but a tail towards the large-particle side. The shape of distribution curve is typically indicative of a crystallite migration and coalescence particle growth mechanism during preparation [12,13]. However, the agglomeration of the Pt particles in HCHO-L was significant, as indicated in Fig. 1(d). Some Pt particles grow up to at least 100 nm. Corresponding size distribution histogram indicates a broad and bimodal distribution with average sizes of 1.5–500 nm.

Fig. 2 compares XRD patterns of the 40 wt.% Pt/C samples. It can be seen that the broadening of the XRD peak becomes apparent for these samples, with the exception of the sample HCHO-L. Although XRD measurements cannot supply exact information of metal particle with crystallite size less than 3.0 nm, the results of XRD measurements qualitatively show that the Pt particle size of HCHO-L sample is much larger than that of other samples. This result is consistent with the TEM analysis. In addition, it is noteworthy that X-ray diffraction of HCHO-L sample only gives statistical results and diffraction information of small Pt particles in the range of 1.5–6 nm cannot be presented.

The chemistry of preparation process of supported platinum catalysts with low loadings has been well understood [15,16]. In that case, most of Pt precursor is strongly chemisorbed at the walls of the carrier's pores before reduction. However, the chemistry involved in the preparation of metal catalysts with high metal loadings is still unknown. Fundamental study concerning steps of redox reaction and nucleation is needed to understand the chemistry of each process. UV–vis spectrophotometry was applied to follow the reduction in both processes. Colloidal dispersions of metals exhibit absorption bands or broad regions of absorption in the UV–vis range. These are due to the excitation of plasma resonances or interband transitions and is a characteristic property of the metallic nature of the particles [17]. As demonstrated in Fig. 3, UV–vis spectroscopy measurements show that the typical absorption of $PtCl_6{}^{2-}$ at 260 nm completely disappeared in the aqueous impregnation route whether short or long impregnation time was adopted [18]. The typical absorptions of Pt^{2+} at 220 nm and Pt colloid at 215 nm coexist in the solution after immersed for 15 min [19], suggesting that a two-step reaction mechanism is involved where $PtCl_4{}^{2-}$ serves as an intermediate. Namely,

$$PtCl_6{}^{2-} + HCHO + H_2O \rightarrow PtCl_4{}^{2-} + HCOOH + 2H^+ + 2Cl^- \quad (1a)$$

$$PtCl_4{}^{2-} + HCHO + H_2O \rightarrow Pt^0 + HCOOH + 2H^+ + 4Cl^- \quad (1b)$$

Only weak absorption of Pt colloid at 215 nm appears in the solution after 36 h impregnation, indicating that the redox reaction can be completed at a slow rate under ambient conditions via the two-step reaction path. Comparatively, formaldehyde is a relatively strong reducing agent. The redox reaction, as showed in Eq. (1), takes place with a slow rate at relatively low temperature. Thus, a few Pt nucleus may be formed at first in the suspension, on which following reduced platinum deposited through autocatalytic pathway resulting in the large Pt particles [20]. Therefore, a slow reaction rate has to be avoided to obtain high dispersion of supported Pt-based electrocatalysts with strong reducing agent but without using stabilizing agent.

However, the situation does not occur at ambient temperature when the relatively weak reducing agent, ethylene, glycol is used. The examination of reaction system in the polyol process by UV–vis spectroscopy shows no detectable change even after 3 h in ambient conditions. But the reaction rate in polyol process increases with reaction temperature apparently. The absorption of $PtCl_6{}^{2-}$ at 264 nm decayed slowly during the first 5 min at 60 °C, while the absorption at 220 nm was not observed, as demonstrated in Fig. 4. After the induction period of 5 min, the absorption of $PtCl_6{}^{2-}$ markedly decreased and finally disappeared after 45 min. Therefore, the reduction of Pt ions by ethylene glycol is probably autocatalytic at the particle surfaces. When the reaction system remains at 100 °C from the beginning

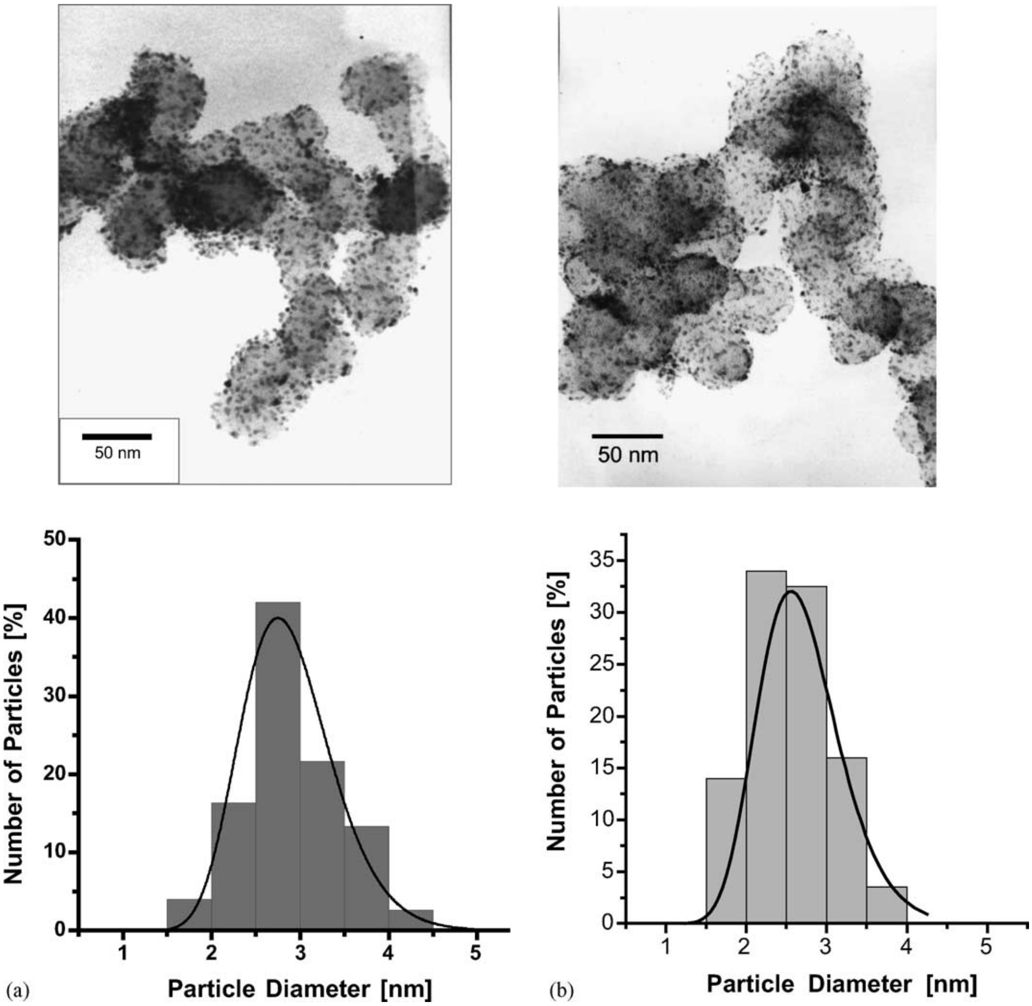

Fig. 1. TEM images of 40 wt.% Pt/C and their corresponding size distribution histograms: (a) EG-S; (b) HCHO-S; (c) EG-L; (d) HCHO-L.

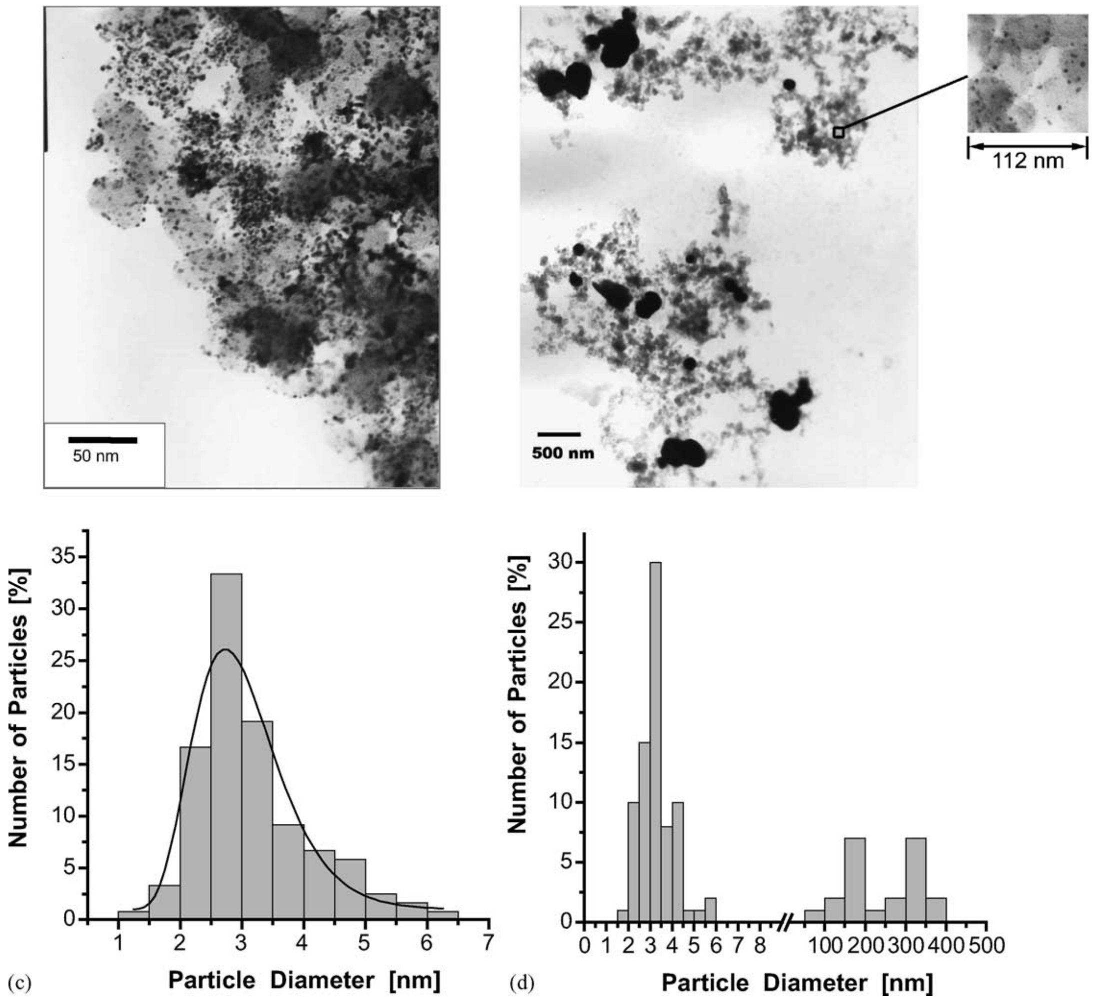

Fig. 1. (*Continued*).

of the reduction, the complete disappearance of the Pt ions absorption is shorten to 2 min. With microwave irradiation,[1] the reaction time to complete the redox process was shorten further to about 16 s. Therefore, it is possible that the modified polyol process can effectively control particles size and distribution at relatively high reaction temperature because of its fulfillments of two conditions: quick nucleation and a complete separation of the nucleation and growth steps [21,22].

UV–vis spectroscopy is also an efficient tool to quantify the concentration of $PtCl_6^{2-}$ anion since the intensity of the absorption peak at ∼260 nm is linearly sensitive towards the $PtCl_6^{2-}$ concentration. Prior to the quantifying measurements, a series of H_2PtCl_6 standard samples with identified concentration were measured to determine the linear relationship between $PtCl_6^{2-}$ concentration and absorption intensity, and then the standard line was plotted. Thus the $PtCl_6^{2-}$ concentration in solution can be quantified by the intensity of the sharp absorption peak at ∼260 nm. As listed in Table 1, UV–vis quantity measurements reveals that the adsorption capacity of carbon black is only 61.17 mg Pt/g carbon in aqueous and 33.3 mg Pt/g carbon in ethylene

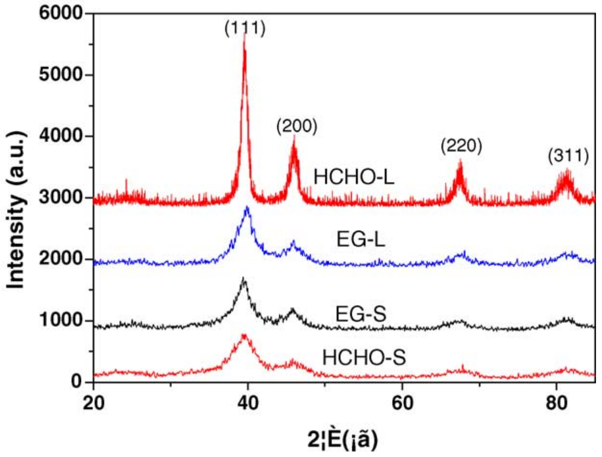

Fig. 2. X-ray diffraction patterns of 40 wt.% Pt/C electrocatalysts prepared by different routes.

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[1] The 30 ml of mixture irradiated with a microwave oven (National NN-S568WFS, 2450 MHz, 900 W).

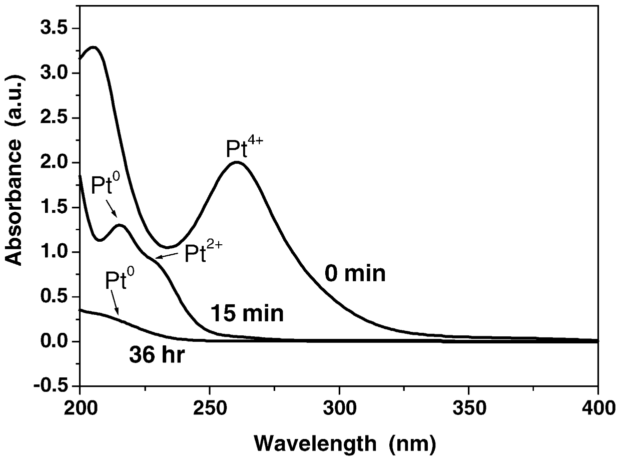


Fig. 3. UV–vis spectrum of a filtrate at various impregnation times. The initial solution contained 1.89×10^{-4} mol/L $H_2PtCl_6 \cdot 6H_2O$ in water.

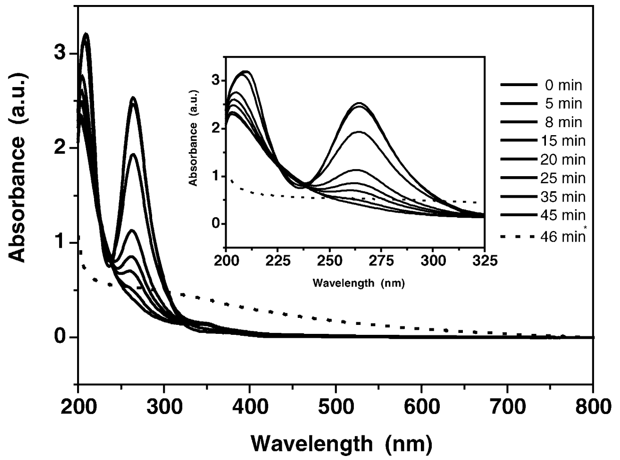
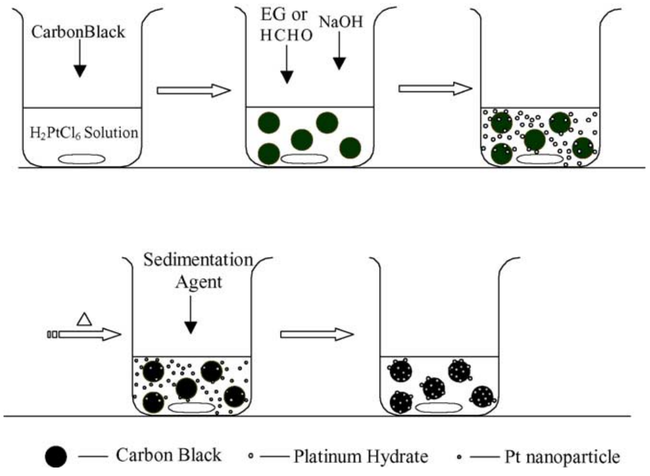


Fig. 4. UV–vis spectrum of a solution at various reduction times. The initial solution contained 9.65×10^{-5} M $H_2PtCl_6 \cdot 6H_2O$ and ethylene glycol/water (1/1, v/v). Spectra from 200 to 300 nm were amplified on the right upper corner. Solid line: absorption intensity decrease with reaction time; Dash line: after 45 min redox reaction at 60 °C, solution was remained in 130 °C oil bath for 1 min more.



Scheme 1. The proposed mechanism of both impregnation methods.

glycol after adsorption equilibrium is reached. That means 91 wt.% of $PtCl_6^{2-}$ ions suspended in the aqueous solvent, while 95 wt.% of $PtCl_6^{2-}$ ions in ethylene glycol solvent. In addition, the absorption of Pt colloid at 215 nm in the reaction solution in aqueous impregnation process can be observed after 15 min immersion at room temperature, as indicated in Fig. 3. Moreover, TEM analysis shows that most of Pt nanoparticles suspended in the reaction solution in polyol process. Based on these facts, it can be concluded that the nucleation of the metallic phase and the growth of the individual nuclei occur mainly in the liquid phase and partly on the carbon support, as illustrated in Scheme 1. This is quite different from the case of low metal loadings where Pt precursor is adsorbed strongly on carbon in the impregnation step [14]. From this point of view, the principles in the colloid and interface chemistry may be followed for the preparation of supported metal catalysts with high loadings. The well-known LaMer diagram schematically described that one brief outburst of nuclei and subsequent uniform growth would finally produce monodispersed system [23]. In addition, the autocatalysis effect should be taken into account for preparation of noble metal colloid, i.e., the redox reaction rate can be increased by reducing the activation energy once the reaction have been initiated. Thus the preparation of ultrafine and monodispersed Pt particles requires that a high number of initial nuclei is presented by a fast redox rate. Such fundamental understanding of nucleation and redox reaction provides critical information for optimizing the synthesis parameters, and helps in design and preparation of supported Pt catalysts with high loadings.

Table 1
Adsorption capacity of carbon black towards Pt ions in different solvents

Solvent	Adsorption capacity (mg Pt/g carbon)	Mass percentage of Pt in solution (wt.%)
EG	33.3	95
H_2O	61.2	91

The electrocatalytical activities of the four 40 wt.% Pt/C electrocatalysts were tested as cathode electrocatalysts in a $30 \times 30\,mm^2$ fuel cell. Fig. 5 shows that the single cell performance with HCHO-S catalyst as cathode electrocatalysts is comparable to that of EG-S catalyst, both of which exhibit slightly better activities than that of EG-L catalyst. Whereas, the single cell performance with HCHO-L catalyst as cathode electrocatalysts is relatively poor. Apparently, higher dispersion of platinum on carbon achieves better electrocatalytic activity for oxygen reduction, indicating that the mass activity of the electrocatalyst increases with Pt surface area. The platinum crystallite size effect for oxygen reduction has not been observed in our study [24], which is consistent with Watanabe's publications [25,26]. At least, the specific activity is independent of the particle size when Pt particle is larger than 2.6 nm.

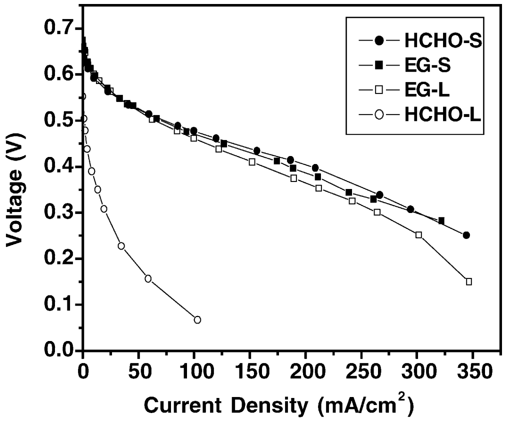


Fig. 5. Performance of single DMFC with different cathode electrocatalysts. Operation conditions: cell temperature: 75 °C; methanol concentration: 1.0 mol/L; flow rate: 1.0 ml/min; oxygen pressure: 0.2 MPa; metal loading in anode: 2.0 mg Pt Ru/cm^2 (20 wt.%Pt-10 wt.%Ru/C, Johnson Matthey Inc.); (metal loading in cathode: 1.0 mgPt/cm^2; Nafion-115.

4. Conclusions

High dispersion of platinum on carbon can be obtained by two different impregnation routes—the improved aqueous impregnation method and the modified polyol process. Although both methods follow very similar routes, impregnation time has significant effect on the particle size and its distribution in improved aqueous impregnation method and low influence in the modified polyol process. That result suggests that the reducing ability and the solvent effect of different agents play important roles in the preparation. In addition, UV–vis spectroscopy measurements qualitativley and quantitively showed that the chemistry of preparation process of Pt/C with high loadings was quite different from that of low loadings. In the case of high metal loadings, most of the Pt nanoparticles firstly formed in solution, then deposited on support. The performance test of single cell demonstrates that the electrocatalyst with higher Pt dispersion has better electrochemical activity.

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