Research Article

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Correlation between electrochemical performance degradation and catalyst structural parameters on polymer electrolyte membrane fuel cell

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Abstract: The catalysts performance degradation is a crucial issue in decay of the polymer electrolyte membrane fuel cell (PEMFC). The effect of Nafion content, dispersity of Pt nanoparticles and selected types of carbon support on the degradation of electrochemical surface area (ECSA) and double layer capacitance (DLC) were experimentally discussed by accelerated stress test (AST). The catalyst with 20wt% Nafion content exhibited better catalyst performance, i.e., the less DLC and ECSA degradation during AST. Catalysts with well Pt dispersity showed superior %ECSA (the percentage change of ECSA) retention. The heat-treated catalysts exhibited the lowest ECSA and DLC degradation rate due to the larger Pt particle and high carbon corrosion resistance. Moreover, a multi-order model describing the correlation between ECSA and DLC degradation was proposed, providing a vital reference for quantitatively investigating ECSA and DLC degradation in the catalysts with different catalysts structural parameters.

Keywords: polymer electrolyte membrane fuel cells; electrochemical surface area loss; carbon corrosion; catalyst structural parameters; catalysts performance degradation

1 Introduction

The global fossil fuel crisis and environmental issues promote the rapid development of new energy solutions [1–3]. Polymer electrolyte membrane fuel cells (PEMFCs) are widely accepted as a kind of new energy devices [4] due to their unprecedented efficiency, zero emission, high reliability, and relative silence [5, 6]. Performance, durability and cost are main challenges for popularization of PEMFCs vehicles. The lifetime target of the United States Department of Energy (US DOE) for 2020 is 5,000 h for transportation power systems [7]. However, PEMFCs vehicles only reach a fraction of lifetime, i.e., 2,500–3,000 h [8], which is far from the commercializing requirement. The performance degradation of PEMFCs is the primary cause of the short service time [9].

The catalysts performance degradation is a crucial issue in PEMFCs performance decay. Several performance degradation mechanisms in catalysts degradation includes (i) electrochemical Ostwald ripening, (ii) Pt migration and coalescence, (iii) Pt detachment from carbon support corrosion, and (iv) Pt dissolution and re-precipitation inside the ionomer phase [10]. Pt particle failures result in the reduced number of catalysts active sites [11]. Carbon support is prone to oxidation at high potentials, especially at PEMFCs cathodes [12]. Carbon corrosion weakens the Pt-C particles and leads to Pt agglomeration [13] or dissolve into electrolyte to increase resistance [14]. Moreover, carbon corrosion could reduce the catalysts layer thickness and change porosity [11], which results in mass transport loss [15].

An accelerated stress test (AST) is designed to evaluate electrochemical surface area (ECSA) and double layer capacitance (DLC) under specified potential range, which is an experimental measure of catalyst performance degra-
The change in ECSA of catalyst during AST was assigned to the change in the number of active sites due to the Pt dissolution, detachment, and migration etc. [16]. The DLC was characterized by the difference between cathodic and anodic currents on the active electrode area without any Faradaic reaction [17, 18]. The variation of DLC during AST attributed to the carbon support corrosion. Reid et al. [19] carried out the AST on two commercially available Pt-based catalysts. An expression between pseudo-capacitance and the ECSA was proposed and used to effectively determine ECSA values without running cyclic voltammogram (CV). Sharma and Andersen [20] attempted to quantify the ECSA degradation mechanisms during an AST of a PEMFC catalyst layer by performing on three-electrode cells. The decrease of DLC was induced by the carbon surface area loss and the oxidation of carbon–oxygen surface groups to CO/CO$_2$ [21, 22]. However, none of previous studies specifically clarify the correlation between ECSA and DLC degradation, which applies to analyze the effect of catalyst structural parameters on performance degradation.

This paper investigated the effect of Nafion content, dispersity of Pt nanoparticles and selected types of carbon support on catalysts performance degradation. Depending on experimental results, their correlation between ECSA and DLC degradation was established, which is the reference to optimize the catalyst structure and advance the PEFMCs technology.

2 Experimental methods

2.1 Catalysts preparation

Chemicals and materials

The commercial carbon black Vulcan carbon was purchased from Carbot (USA). 99.9% Methanol (CH$_3$OH) was obtained from Acros Organics (Belgium). Dihydrogen hexachloroplatinate (IV) hexahydrate (H$_2$PtCl$_6$·6H$_2$O) and commercial 20wt% Pt/C catalyst used here were obtained from Alfa Aesar (UK). 5 wt% Nafion solution was purchased from Sigma Aldrich (USA). 99.5% absolute ethanol, 35% hydrochloric acid (HCl), 95%-98% sulfuric acid (H$_2$SO$_4$) and 69% concentrated nitric acid (HNO$_3$) were purchased from Beijing chemical plant (China). 99% Ethylene glycol (EG) and urea were obtained from Innochem (China).

Preparation of Pt catalysts

The synthesis methodology of carbon-supported Pt nanoparticles was based on Ref. [23]. The uniform reduction of Pt on carbon support was realized by applying EG in a polyol process with a gradual increase of pH realized in situ hydrolysis of urea. Initially, 60 mg of urea was dissolved in 40 mL of deionized (DI) water. Then, 22.7 mg of Vulcan carbon (VC) was added. The mixture was sonicated for 30 min and then 5 mL of 0.01 M H$_2$PtCl$_6$·6H$_2$O solution was added. After intensive stirring for 3 hrs at room temperature, the suspension was heated to 90°C in water bath and kept stirring for 1 h. When cooling to room temperature, 40 mL of EG was added and stirred for 3 hrs at room temperature. Next, the solution was heated to 120°C in an oil bath and stirred for 1 h. Finally, the mixture was cooled to room temperature and stirred overnight. The collected product was washed by DI water and dried at room temperature overnight. Pt/VC catalysts without and with urea-assistant were synthesized, namely, Pt/VC(None) and Pt/VC(Urea), respectively.

Thermal treatment

The prepared 30 mg catalyst Pt/VC(Urea) with good Pt dispersion was submitted to a thermal treatment in a tubular oven OTF-1200X. The sample was placed into porcelain combustion boats and heated during 2 hrs at the selected temperature (500°C, heating ramp and cooling ramp: 10°C min$^{-1}$) under Ar stream supplied by gas supply system (GSL-3F).

N-doped carbon treatment

Briefly, 3 g of VC was dissolved in 300 mL 1 M HCl by magnetic stirring for 24 hrs at room temperature to remove trace metal impurities. The carbon mixture solution was filtered and washed with DI water until pH was neutral. It was dried overnight at 90°C in the air. Then, the pre-treated VC was put in 200 mL HNO$_3$ and the mixture was heated to 90°C by water bath for 5 hrs, and magnetic stirring simultaneously to make it uniform and conduct condensation pipe reflux. After that, it was washed and dried again. Finally, the oxidized VC was in N-doped processed, i.e., spreading the obtained carbon in a crucible and put it in a tube furnace for heating to 400°C at a rate of 5°C /min$^{-1}$. N$_2$ was slowly purged and purified firstly, then NH$_3$ was continuously injected at 10 L/h$^{-1}$. After the temperature was up to 400°C, the sample was held for 2 hrs.
under \( \text{NH}_3 \) atmosphere, after that, the sample was naturally cooled to room temperature under \( \text{N}_2 \) atmosphere.

### 2.2 Characterizations

The morphology of these catalysts was characterized by transmission electron microscopy (TEM, JEOL JEM-2010, Japan) operating at 200 kV acceleration voltage. The TEM sample was prepared from a suspension of catalysts. The catalysts powder was dissolved in ethanol solution by sonication for 1 h to disperse any agglomeration. Subsequently, one drop of the suspension was placed on typical holey carbon-supported Cu TEM grids. The samples were analyzed using TEM in Bright Field mode. The Pt loading on the Pt/C catalysts was measured with thermogravimetric analysis (TG, TA instruments Q600 SDT, USA). The catalysts were heated under air ambient from room temperature to 1000\( ^\circ \text{C} \) with a heating rate of 10\( ^\circ \text{C} \) min\(^{-1}\).

### 2.3 Electrochemical characterization

Electrochemical measurements of prepared catalysts were performed in a standard three-electrode electrolytic cell at room temperature by using a CHI 750E electrochemical analyzer (CHI Instruments, USA). For three-electrode cell, a carbon rod worked as the counter electrode while the potentials were measured using a Hg/Hg\(_2\)Cl\(_2\)/saturated KCl reference electrode. The working electrode was coated with the prepared different catalysts ink. The working electrode was prepared as follows. 1 mg of catalyst was dispersed in 200 \( \mu \text{L} \) of 1:1 (v/v) isopropanol/water mixed solvent under sonication for 1 h to form a homogenous catalyst ink. Then, 3 \( \mu \text{L} \) of the electrocatalyst ink (5 mg mL\(^{-1}\)) was pipetted onto the flat glassy carbon electrode with 3 \( \mu \text{L} \) of 0.25 wt.% Nafion aqueous solution coated on top followed. The coated electrode was then dried at room temperature for 15 min. After that, CV and methanol oxygen reduction (MOR) measurement were performed in a 1 M \( \text{H}_2\text{SO}_4 \) and a mixture of 0.5M \( \text{H}_2\text{SO}_4 \) and 1 M \( \text{CH}_3\text{OH} \) respectively. The area under the hydrogen desorption peak between 0.4 to 1.6 V (vs RHE) at 1 V s\(^{-1}\) for 2,000 cycles in a three-electrode cell with a liquid electrolyte (1 M \( \text{H}_2\text{SO}_4 \)). The ECSA and DLC measurements were performed after 0, 100, 200, 400, 800, 1,000, 2,000 potential cycles and recorded by the CV with the potential ranges of 0.021-0.2 V (vs RHE) at a sweep rate of 50 mV s\(^{-1}\). The carbon corrosion can be estimated through the DLC change of the electrode in the absence of any Faradaic processes. DLC was measured using the average value of difference between the cathodic and anodic currents in the region away from the faradaic reactions (0.3-0.45V vs RHE).

### 3 Results and discussion

#### 3.1 Catalyst morphology and electrochemical performance

Pt/VC catalysts without and with urea-assisted were synthesized and denominated as Pt/VC(None) and Pt/VC(Urea), respectively. The prepared Pt/VC(Urea) was heated at 500\( ^\circ \text{C} \) in \( \text{Ar} \) atmosphere to obtain Pt/VC(HT). N-doped carbon was selected in the preparation of Pt/VC(N-doped) catalysts. The morphology of four different catalysts was characterized by TEM. The histogram of particle size distribution was counted based on 100 nanoparticles. An obvious agglomeration and coalescence of Pt nanoparticles is found in Pt/VC(None) catalysts marked by green circles in Figure 1(a1). On the contrary, Pt/VC(Urea) has a good Pt dispersity on VC with uniform Pt particle distribution (Figure 1(b1)). Both Pt/VC(N-doped) and Pt/VC(HT) have well Pt dispersity (Figure 1(c1 and d1)). These prepared catalysts have a relatively narrow size distribution between 2 and 7 nm (Figure 1(a2-d2)). The order of average Pt particles size of catalysts is Pt/VC(Urea) (2.17 nm) < Pt/VC (None) (3.08 nm) < Pt/VC(N-doped) (3.62 nm) < Pt/VC(HT) (7.28 nm). Pt/VC(HT) possess the largest Pt particle size is probably due to agglomerated growth of small nanoparticles during a thermal treatment. Pt content was detected by TG measurement with the value of 23.61wt% for Pt/VC(None), 28.8wt% for Pt/VC (Urea), 33.18wt% for Pt/VC(N-doped) and 39.08wt% for Pt/VC(HT), respectively. The value is close to the theoretical value of 33wt%. While, the Pt content in Pt/VC(HT) exceed 33wt% possibility resulted from the loss of carbon mass during the thermal treatment.

The electrochemical performance characteristics of the four types of catalysts are significantly different (Figure 2). ECSA is investigated by calculated charge trans-
Figure 1: TEM images and Pt size distribution of (a) Pt/VC(None), (b) Pt/VC(Urea), (c) Pt/VC(N-doped), and (d) Pt/VC (HT)

- Pt/VC(None) average size: 3.08 nm
- Pt/VC(Urea) average size: 2.17 nm
- Pt/VC(N-doped) average size: 3.62 nm
- Pt/VC (HT) average size: 7.28 nm
ferred during hydrogen desorption in the potential range of 0.02 – 0.427 V (vs RHE) in 1 M H₂SO₄ (Figure 2(a1)). The Pt/VC(Urea) with good Pt dispersity gives a very high value of ECSA (89 m² g⁻¹). This value is 1.4 times higher than that for Pt/VC (None) (65 m² g⁻¹), 1.5 times higher than that for Pt/VC(N-doped) (60 m² g⁻¹), and 2.3 times higher than that for Pt/VC(HT) (38 m² g⁻¹) (Figure 2(a2)). The ECSA decrease with the increase of average Pt particle size due to the decrease of current intensity for the hydrogen desorption peak. The electrochemical performance toward methanol oxygen reduction (MOR) is investigated in a mixture of 0.5 M H₂SO₄ and 1 M CH₃OH (Figure 2(b1)). Two typical peaks during the forward and backward sweeps are observed at the potential of 0.9 V and 0.7 V, respectively. The Pt/VC(Urea) exhibits better catalytic performance than either the Pt/VC (None), Pt/VC(N-doped) or Pt/VC(HT). The mass activity of Pt/VC(Urea) (1.3 A mg⁻¹) is 1.3 times higher than that of Pt/VC(None) (1.0 A mg⁻¹), 1.1 times higher than that of Pt/VC(N-doped) (1.2 A mg⁻¹), and 1.6 times higher than that of Pt/VC(HT) (0.8 A mg⁻¹) (Figure 2(b2)). These results clearly demonstrated that Pt/VC(Urea) exhibits higher catalytic activities than Pt/VC(None), Pt/VC(N-doped), and Pt/VC(HT) in terms of both ECSA and mass activity.

### 3.2 Effect of Nafion content on catalyst performance degradation

Catalysts performance degradation of Pt/C catalysts was investigated according to the potential cycles test between 0.4 and 1.6 V. To compare the degradation of ECSA and DLC obtained in all catalysts, the percentage change of catalysts is normalized with respect to its initial state value of DLC and ECSA. Thus, the following equations are used:

\[
\%\text{ECSA} = \frac{\text{ECSA}_{n-th\ cycle}}{\text{ECSA}_{BOL}} \times 100\%
\]
Figure 3: Variations of (a) % ECSA and (b) % DLC with potential cycling for catalysts with different Nafion contents

\[
\%\text{DLC} = \frac{\text{DLC}_{n-th\ cycle}}{\text{DLC}_{BOL}} \times 100\%
\]

where ECSA_{BOL} and DLC_{BOL} are the ECSA and DLC values of the beginning-of-life catalysts and ECSA_{n-th\ cycle} and DLC_{n-th\ cycle} are the ECSA and DLC after the n-th potential cycles.

The calculated %ECSA and %DLC of Pt/VC catalysts against the number of potential cycles are plotted in Figure 3. The 20wt%, 40wt%, and 60wt% Nafion content are choose. The 20wt% Nafion content in catalysts ink shows a little bit slow decreasing rate in ECSA degradation (Figure 3a) and a higher %DLC retention, i.e., exhibits a little bit high corrosion resistance (Figure 3b). It accords with the reported catalysts with optimal Nafion ionomer content around 25wt% [24]. By contrast, the %ECSA and %DLC results of catalysts with 60wt% Nafion content exhibits an evidently reduction trend. An excess supply of Nafion ionomers content on catalyst may wrap catalyst and block the catalyst sites that results in the decreasing of the porosity of catalysts and the mass transport.

3.3 Effect of Pt dispersity on catalyst performance degradation

The uniform reduction of Pt on carbon was realized by urea-assisted synthesis method. Pt/VC catalysts without and with urea-assisted were synthesized and denominated as Pt/VC(None) and Pt/VC(Urea) respectively. Pt/VC(None) exhibits a little bit rapid %ECSA reduction trend (the 14% retention of ECSA) than Pt/VC(Urea) (the 18% retention of %ECSA) (Figure 4a) due to Pt aggregation on carbon support showed in Figure 1(a1). Meanwhile, more rapid %DLC reduction trend is found in Pt/VC(None),
and the %DLC retention (88%) is smaller than that of Pt/VC(Urea) (92%) (Figure 4b). The Pt/VC(Urea) with good Pt dispersity exhibits slower ECSA and DLC degradation. There is residual urea in catalysts after the preparation of Pt/VC(Urea) catalysts by urea-assisted synthetic method. The hydrolysis of urea to raise the pH is sufficiently to form a stable protective film on carbon surface to mitigate the corrosion [25].

### 3.4 Effect of selected types of carbon supports on catalyst performance degradation

The catalysts (Pt/VC(HT)) were prepared by heated treatment in Ar flow at 10°C/min from room temperature to 500°C. The Pt/VC(N-doped) catalysts with N-doped VC was used for comparison. The ASTM results show that both the un-doped VC and the N-doped VC supported Pt particles exhibit similar ECSA degradation over the potential cycles (Figure 5a). While, Pt/VC(HT) shows the less ECSA degradation with the highest retention of %ECSA (24%) among these catalysts (Figure 5a). It attributes to the larger Pt particle size of 7.2 nm in Pt/VC(HT) with low surface area and thermodynamic stability which tends to be more stable [26]. The smaller Pt particle size is prone to more severe Pt dissolution [10]. Moreover, Pt/VC(HT) exhibits the highest %DLC retention (94%) (Figure 5b). The thermal treatment made VC become high corrosion resistance and exhibited 6% increase in %DLC retention due to the enhanced hydrophobicity and crystallinity of the carbons by thermal treatment [27].

### 3.5 Empirical model of the catalyst performance degradation mechanism

To further understand the catalyst performance degradation mechanism, the correlations between ECSA and DLC degradation of different catalysts was investigated. The %DLC vs %ECSA test plots of catalysts with different Nafion content were firstly investigated. These curves show an apparent decay during 2,000 potential cycles. Catalysts with 20 wt% Nafion content exhibits a lowest reduction trend. While, catalysts with 60 wt% Nafion content has an evidently reduction. The excess Nafion ionomers can block the catalyst sites, resulting in the decrease of the porosity of catalysts and the mass transport. In the same way, the curves of %DLC vs %ECSA in catalysts with different Pt dispersity and selected types of carbon supports were concluded then. The Pt/VC(HT) exhibits the highest %DLC and %ECSA retention among these catalysts. It attributes to enhanced carbon corrosion resistance and catalysts structure by thermal treatment.

The degradation curves can be expressed as the multi-order model as follows:

\[
\ln(\%\,\text{DLC}) = k \cdot (\%\,\text{ECSA})^n + b
\]

where %DLC, %ECSA indicate as DLC and ECSA degradation, respectively. \(k\) represents the multi-order rate constant. \(n\) denotes as catalysts degradation rate, and \(b\) denotes as carbon corrosion resistance coefficient. The values of the \(k\), \(n\), and \(b\) were calculated and given in Table 1. The R-square \((r^2)\) of most of the curves are ranged from 0.98-0.99, that demonstrate the well agreement of the model to experimental data.

The fitted constant \(k\) in catalysts with different Nafion content is \(3.347 \times 10^{-4}\), in Pt dispersity and selected types
Figure 6: The %DLC vs %ECSA test plots of catalysts with different (a) Nafion contents, (b) Pt dispersity and selected types of carbon supports

Figure 7: Degradation curves of catalysts with (a) different Nafion contents, (b) Pt dispersity and carbon support in different treated types by the multi-order model Eq. (4)

Table 1: The fitted values of $k$, $n$ and $b$ from Eq. (4) of all catalysts

| Catalysts      | Nafion content (wt%) | $k$    | $n$    | $b$    |
|----------------|----------------------|--------|--------|--------|
| Commercial Pt/C| 20                   | $3.347 \times 10^{-4}$ | 1.28   | 4.479  |
| Commercial Pt/C| 40                   | $3.347 \times 10^{-4}$ | 1.30   | 4.463  |
| Commercial Pt/C| 60                   | $3.347 \times 10^{-4}$ | 1.35   | 4.431  |
| Pt/VC(HT)      | 20                   | $3.123 \times 10^{-8}$ | 3.13   | 4.545  |
| Pt/VC(Urea)    | 20                   | $3.123 \times 10^{-8}$ | 3.20   | 4.520  |
| Pt/VC(None)    | 20                   | $3.123 \times 10^{-8}$ | 3.30   | 4.482  |
| Pt/VC(N-doped) | 20                   | $3.123 \times 10^{-8}$ | 3.32   | 4.468  |

of carbon supports is $3.123 \times 10^{-8}$. With the increasing of $n$, the catalysts degradation rate is more rapid. According to fitted curves, catalysts with 20wt% Nafion content has the minimum value of $n$ (1.28) because of slowest ECSA and DLC degradation (Figure 7a). As the fitted degradation curves shown in Figure 7b, Pt/VC(HT) has the minimum value of $n$ (3.13) that exhibits the highest %ECSA and %DLC retention. In addition, Pt/VC(HT) has the maximum value of $b$ (4.545) in these catalysts due to the heat-treated VC exhibiting high corrosion resistance. The established correlation by multi-order model can simplify the qualitative analysis of catalysts degradation behavior. The degradation behavior of catalysts with more wide range of Nafion content can be further discussed with the fitted constant $k$. By means of this model, other catalysts structural parameters (e.g. the Pt loading, carbon loading, and different types of carbon in catalyst) will be further investigated to understand the effect of structural parameters on catalysts degradation.
4 Conclusions

In this paper, the effects of Nafion content, Pt dispersity, and selected types of carbon supports on catalysts performance degradation were discussed. Experimental results of AST showed that the catalyst with 20 wt% Nafion content exhibits superior catalyst performance, i.e., the less DLC and ECSA degradation. The uniform reduction of Pt on carbon (Pt/VC(Urea) realized the high %ECSA and %DLC retention after AST. Pt/VC(HT) had the lowest ECSA and DLC degradation due to the larger Pt particle and high carbon corrosion resistance after thermal treatments. Moreover, a multi-order model was proposed to describe the correlation between ECSA and DLC degradation. By means of this model, different catalysts structural parameters (e.g. the Pt loading, carbon loading, and different types of carbon in catalyst) can be investigated to guide catalyst structure optimization as well as to enhance the performance degradation resistance.

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