Polyaniline/Platinum Composite Cathode Catalysts Towards Durable Polymer Electrolyte Membrane Fuel Cells

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Polymer stabilization proved to be a promising approach to increase the catalytic performance of common platinum/carbon based cathode catalysts (Pt/C) used in polymer electrolyte membrane fuel cells (PEMFCs). Platinum and polyaniline composite catalysts (Pt/C/PANI) were prepared by combining chemical polymerization reactions with anion exchange reactions. Electrochemical ex-situ characterizations of the decorated Pt/C/PANI catalysts show high catalytic activity toward the oxygen reduction reaction (ORR) and, more importantly, a significant enhanced durability compared to the undecorated Pt/C catalyst. Transmission electron microscopy (TEM) investigations reveal structural benefits of Pt/C/PANI for ORR catalysis. All studies confirm high potential of Pt/C/PANI for practical fuel cell application.

The durability of polymer electrolyte membrane fuel cells (PEMFCs) is one of the key factors to be addressed regarding their successful commercialization. Among lifetime limiting effects, electrocatalyst degradation is one major contributor causing excessive loss of stack voltage. In almost all PEMFC devices, platinum based nanoparticles finely dispersed on a carbon support material (Pt/C) are widely used as electrocatalyst. Besides its superior electrical and resistance characteristics, Pt as metal possesses distinctive ability in catalyzing partial reactions of important molecules that are essential for many industrial processes. Although being the most active metal enhancing fuel cell reaction kinetics, Pt is not stable when being subjected to high acidity, high potential, alternating humidity and temperatures during fuel cell operation. As a result, the catalyst’s electrochemical active surface area (ECSA) loss due to carbon support corrosion, Pt nanoparticle dissolution and agglomeration denote typical fuel cell failure. Designing highly efficient, durable and reliable electrocatalysts is vital in advancing future fuel cell technology.

Substantial efforts have been dedicated to the establishment of long-lasting catalyst systems through polymer stabilization. Polyaniine (PANI) belongs to the family of conducting polymers owing benefits like high electric conductivity, high proton conductivity, good corrosion resistance and environmental stability. But, especially its extended π-conjugated structure that ensures unique redox properties and electron conductivity make it a promising material for electrocatalysis.

This article presents the modification of a Pt/C catalyst using surface coatings of PANI specifically to improve catalyst durability. Simultaneously, PANI favors the catalysis of the oxygen reduction reaction (ORR) as the polymer chains are expected to promote oxygen (O₂) species mobility.

PANI coated Pt/C catalysts (denoted Pt/C/PANI) were prepared in a straightforward two-step synthesis procedure (Scheme 1). First, the carbon support was embedded in a layer of PANI via oxidative polymerization of aniline monomers. Second, Pt nanoparticles dispersed on the coated carbon support were obtained by means of bromide anion exchange reaction.

In the course of the synthesis route of this stabilization method, the PANI layer preferentially covers the surface of the carbon support rather than that of Pt, hence not sacrificing any catalytic activity. Considering the enhancement of catalytic performance, the polymer plays three important roles. During the polymerization, aniline monomers are adsorbed onto the carbon support surface via π–π conjugation and further polymerized to a thin PANI layer which acts as some kind of a protector as it saves the carbon support from direct exposure to the corrosive environment in the fuel cell. Thus, carbon corrosion is distinctly inhibited.

Also, the PANI film strengthens the interaction between the Pt and the carbon support as well as it provides special separation of the Pt particles minimizing Pt dissolution and agglomeration, respectively.

Last, due to electron delocalization between the Pt d-orbitals and the π-conjugated polyaromatic system of PANI the
The electronic configuration of Pt is changed. The resulting lowered d-band center and raised energy level favor the electron transfer between Pt/C/PANI and O₂ because of a reduced gap between the O₂ LUMO (lowest unoccupied molecular orbital) and the Pt/C/PANI catalyst HOMO (highest occupied molecular orbital). Therefore, the desorption of O₂ intermediate species on the catalyst surface is facilitated during the ORR.⁴,⁵,¹²

The electrochemical behavior of various Pt/C/PANI catalysts compared to the uncoated Pt/C reference catalyst was characterized performing cyclic voltammetry (CV) and ORR measurements by means of rotating disk electrode (RDE) technique.⁶

The investigations confirm excellent catalytic activity and durability being attributed to the unique catalyst structure of various Pt/C/PANI catalyst samples. However, activity highly depends on the thickness of the PANI layer, which is selected through the concentration of aniline monomers in the first synthesis step. Figure 1a shows cyclic voltammograms (CVs), recorded in a N₂ saturated 0.1 M HClO₄ electrolyte, of Pt/C/PANI catalysts with different PANI contents of 30, 20, 10 and 50% adjusted to a Pt content of 50%. The ECSA was calculated by measuring the coulombic charge for hydrogen adsorption/desorption after double layer correction considering 210 μC cm⁻² as conversion factor.⁷,⁸ The trend of decreasing ECSA with increasing PANI content might suggest that a high PANI content could incorporate the Pt nanoparticles into the polymer film and block catalytically active sites.

Between 0.4-0.8 V vs. RHE, the CV of Pt/C/PANI (50%) shows typical peaks appearing in the CV of pure PANI, which indicates the PANI content being too high and covering the Pt particles.⁹ On the opposite, a low PANI content does not lead to any functionality.

To investigate ORR activity, polarization curves were recorded in O₂ saturated 0.1 M HClO₄ electrolyte at a rotation rate of 1600 rpm. Figure 1b depicts that the current peak obtained from Pt/C/PANI (30%) shifts toward more positive potential by more than 60 mV relative to the Pt/C reference catalyst. This shift and consequently the enhanced catalytic activity may correlate with a weak adsorption and enhanced desorption of O₂ species on the Pt/C/PANI surface that has been shown to be favorable to an increased catalytic activity toward the ORR. On the contrary, potential shift toward more negative potential cannot confirm any improvement in catalytic behavior.

The mass activity (MA) and the specific current density (specific activity, SA) were calculated at 0.9 V vs. RHE at a rotation rate of 1600 rpm, respectively.⁹,¹³,¹⁴ The calculated values thereof are given in Table 1. These data show that the Pt/C/PANI (30%) catalyst drastically outperforms the other Pt/C/PANI catalyst sample and the Pt/C reference catalyst. Also, the number of electrons exchanged during ORR (e⁻ no.), accounting to four in theory, was calculated by performing Levich analysis.¹⁴

The morphology of the Pt/C/PANI (30%) catalyst was examined by transmission electron microscopy (TEM). Figure 2 clearly exhibits homogenous Pt nanoparticle distribution on the PANI coated carbon support with an average thickness of the PANI layer of 3 nm.

Voltage cycling was used as durability test to investigate the stability of the Pt/C/PANI (30%) catalyst to the Pt/C reference catalyst and carried out by continuously applying linear potential sweeps from 0.6–1.2 V vs. RHE in N₂ saturated 0.1 M HClO₄ electrolyte. The ECSA values for both samples were calculated from the CVs after every 1,000 cycles. Figure 3a shows the CVs of the Pt/C/PANI (30%) and the Pt/C reference catalyst at the beginning of the durability test (begin of life, BoL) and the end of test (end of life, Eol). The normalized ECSA was plotted as function of cycle number (Figure 3b). Thereby, the loss of ECSA for the Pt/C reference catalyst accounts to 82%

| Sample          | MA/A mgPt⁻¹ | SA/mA cm⁻² | e⁻ no. |
|-----------------|-------------|------------|--------|
| Pt/C            | 0.027 ± 0.005 | 0.053 ± 0.0027 | 4.04 ± 0.10 |
| Pt/C/PANI (30%) | 0.063 ± 0.0022 | 0.089 ± 0.0018 | 4.06 ± 0.01 |
| Pt/C/PANI (20%) | 0.037 ± 0.001 | 0.054 ± 0.0009 | 4.30 ± 0.03 |
| Pt/C/PANI (10%) | 0.018 ± 0.001 | 0.030 ± 0.0010 | 4.00 ± 0.01 |
| Pt/C/PANI (50%) | 0.019 ± 0.002 | 0.051 ± 0.0019 | 4.07 ± 0.01 |

Table 1. Summary of the catalytic parameters MA, SA and number of electrons exchanged during ORR of various Pt/C/PANI catalyst samples compared to the Pt/C reference catalyst.
whereas the ECSA of Pt/C/PANI (30%) decreased by only 27% after 10,000 cycles indicating significant higher resistance toward catalyst degradation effects due to the mentioned stabilizing role of PANI within the new catalyst system.

In summary, we have successfully shown in ex-situ experiments that polymer coated Pt/C/PANI catalysts significantly improve the catalytic performance of PEMFCs, especially the ORR activity and stability. The experimental data display that the catalytic performance strongly depends on the thickness of the PANI layer on the carbon support particles and reaches a maximum at an average thickness of 3 nm herein. Compared to the Pt/C reference catalyst, the ORR activity of the Pt/C/PANI (30%) catalyst could be more than doubled and its ECSA loss is three times lower during the durability test. These results are of considerable importance for fuel cell technology in view of the necessary development of highly stable catalysts while improving catalytic performance.

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