

Degradation studies of OMC supported Pt electrocatalyst for PEMFC application in acid electrolyte

Juqin Zeng, Carlotta Francia, Stefania Specchia, Paolo Spinelli

Department of Materials Science and Chemical Engineering, Politecnico di Torino
Corso Duca degli Abruzzi, 24 - 10129 Torino, Italy

Introduction

Proton Exchange Membrane Fuel Cells (PEMFCs) have been extensively developed because of their high power density, low pollution and light weight. Nowadays, high cost of noble catalysts and insufficient durability of the cells are considered to be the major barriers which inhibit the mass commercialization of this promising technology. To meet DOE targets of 2015, about \$30/kW of cell cost and 5000 h of cell operation are required in a vehicle. In order to reduce the amount of precious metal used and increase the stability of catalysts, carbon materials with high surface area are commonly used as catalyst supports for both the anode and the cathode in fuel cells [1]. In the present work, an ordered mesoporous carbon (OMC) with high surface area was employed to support Pt nanoparticles. The interaction between Pt nanoparticles and carbon supports was examined by X-ray photoelectron spectroscopy (XPS). Accelerated aging tests were conducted to evaluate the stability of Pt/OMC catalyst.

Experimental

Materials

An OMC, namely C16_{sucr}, was templated from 3-D cage-like mesoporous SBA-16 silica with sucrose as the carbon precursor [2]. Dispersion of the catalytic metal (Pt) on the OMC was achieved by wet impregnation. A solution of chloroplatinic acid hexahydrated (H₂PtCl₆·6H₂O, Sigma Aldrich) in acetone was added drop by drop to the carbon powder

and stirred for 3 h. After evaporation of acetone at 60°C, the sample was then treated under H₂ flow at 300°C for 2 h in order to reduce the PtCl₆²⁻ ions to metallic Pt. In this work, C16_{sucr} supported catalyst was prepared and denoted as Pt/C16_{sucr}. The platinum percentage in the catalyst was about 11.5 wt. % determined by ICP-AES. Pt/Vulcan XC-72 (10 wt. %, E-TEK) was used as a comparison.

Apparatus and Procedures

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Physical Electronics PHI 5800 (USA) with monochromatic Al-Kα X-ray radiation. The survey and narrow spectra were obtained by passing energy of 187.8 and 23.5 eV, respectively. The samples were placed in an ultra high vacuum chamber at 2 × 10⁻¹⁰ Torr. Platinum percentage in the catalysts was determined by ICP-AES on a Varian Liberty 100 instrument.

Accelerated degradation tests were executed on a workstation (CH Instruments Co., USA) with an Ag/AgCl (1.0 M Cl⁻) electrode and a Pt wire as reference and counter electrode, respectively. Working electrode was prepared with a total Pt loading of 0.012 mg. The working electrode was cycled between 0.2-1.0 V at a scan rate of 1.0 V s⁻¹ in N₂-saturated 0.5 M H₂SO₄ solution. Cyclic voltammograms (CVs) were recorded before cycling and after every 1000 consecutive cycling.

Results and Discussion

XPS was employed to analyze the surface

properties of the catalysts. The XPS spectra are referred to a C 1s value of 284.6 eV. As can be seen from Fig. 1, XPS spectra were dominated by Pt and C signals for both the catalysts. The atomic percentage of oxygen on Pt/C16_{sucr} was 6.6%, which was much higher than 3.6% of oxygen on Pt/Vulcan. The higher oxygen content on the surface of Pt/C16_{sucr} may result from more oxygen-contained functional groups such as carboxyl and hydroxide on the OMC. These surface functional groups are thought to provide active sites for interacting with metal precursors and increase the interaction between the metal particles and the carbon support, resulting in an improved electrochemical stability of Pt/C catalysts [3]. The binding energy of Pt4f peak for Pt/C16_{sucr} increased by 0.19 eV compared to that for Pt/Vulcan, reflecting stronger interaction between Pt nanoparticles and OMC [4]. Potential cycling is a common accelerated degradation test for electrocatalysts. Fig. 2A shows the CVs for Pt/C16_{sucr} and Pt/Vulcan before cycling and after every 1000 consecutive cycling. The ECSA of electrocatalysts was calculated from hydrogen desorption peaks. The percentages of the residual ECSA of catalysts were calculated and shown in Fig. 2B. The ECSA residual was expressed by $ECSA/ECSA_{ini}$, where $ECSA_{ini}$ was the initial electrochemical active surface area of the catalysts and ECSA was the one after cycling. After 4000 potential cycles, the loss of ECSA for Pt/Vulcan was (27.5%), more than twice of that for Pt/C16_{sucr}, revealing that the Pt/C16_{sucr} possessed higher

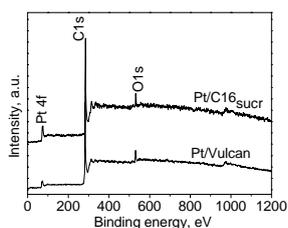


Fig 1. XPS survey of the Pt/C catalysts

stability in acid solution compared with Pt/Vulcan. The higher durability of Pt/C16_{sucr} is likely due to the stronger interaction between Pt and carbon support confirmed by XPS, which minimized the coalescence and Ostwald ripening of small Pt nanoparticles [5]. The higher specific surface area of C16_{sucr} support could also be helpful to confine the sintering of Pt nanoparticles.

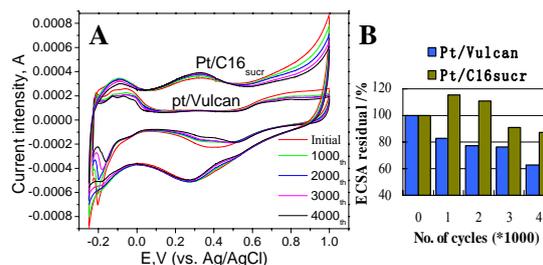


Fig 2. CVs for Pt/C during potential cycling test (A); Percentage of ECSA residual (B)

Conclusion

Ordered mesoporous carbon supported Pt (Pt/C16_{sucr}) electrocatalyst was synthesized and showed higher durability in acid solution compared to commercial Pt/Vulcan. The enhanced stability of Pt/C16_{sucr} can be attributed to the strengthened interaction between Pt nanoparticles and OMC support, effectively precluding the sintering of Pt nanoparticles on OMC.

References

- [1] E. Antolini, Appl. Catal. B: Environ. 88 (2009) 1-24.
- [2] H.I. Lee, J.H. Kim, D.J. You, J.E. Lee, J.M. Kim, W.S. Ahn, C. Pak, S.H. Joo, H. Chang, D. Seung, Adv. Mater. 20 (2008) 757-762.
- [3] W.M. Chen, Q. Xin, G.Q. Sun, Q. Wang, Q. Mao, H.D. Su, J. Power Sources 180 (2008) 199-204.
- [4] H.J. Kim, W.I. Kim, T.J. Park, H.S. Park, D.J. Suh, Carbon 46 (2008) 1393-1400.
- [5] X.G. Li, G. Liu, B.N. Popov, J. Power Sources 195 (2010) 6373-6378.