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An extensive study about influence of the carbon support morphology on Pt activity and stability for oxygen reduction reaction

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ABSTRACT

Several commercial carbons were tested with respect to their thermal stability and electrochemical activity as Pt catalyst support for oxygen reduction reaction (ORR). TGA analysis revealed that carbons with low BET surface such as graphite nanoparticles (GNP_{500}, 100 $m^2 g^{-1}$) are less prone to degradation than ordered mesoporous carbon (OMC, 1000 m^2g^{-1}). Moreover, high Pt loading favored considerably carbon oxidation rate in air. Best results in terms of activity for ORR and stability during electrochemical accelerated degradation tests (ADT) were yielded by Pt/GNP_{500} and Pt/OMC, respectively. High graphitization level and mesoporous surface structure of carbon were found to be determinant for sustainable Pt stability. Addition of certain amount of PTFE to Nafion as binder in gas diffusion electrode (GDE) catalyst layer clearly improved electrochemical surface area (ECSA) retention. Comparative identical location TEM images of electrochemically-aged Pt on Vulcan and OMC demonstrated positive influence of mesoporous carbon surface on immobilization of catalyst particles and consequently on ECSA retention. After 10,000 ADT cycles, ECSA retention was close to 30% for Pt/OMC compared to about 1% for Pt/Vulcan. This was due to dramatic increase of Pt particle size on Vulcan support up to 40 nm compared to about 15 nm for Pt on OMC.

1. Introduction

Direct methanol fuel cell (DMFC) is a promising technology for energy supply of portable and stationary applications due to high energy density of methanol, compact design, easy fuel handling and storage. However, poor activity of Pt for methanol oxidation, low corrosion resistance of Pt/C at high cathodic voltage and methanol crossover that results on fuel loss mixed potential formation at the cathode are technical challenges to overcome [1]. Methanol efficiency up to about 80% can be yielded by using appropriate fuel concentration and applying high current density [2]. Long-term efficiency of the electrodes is strongly influenced by structural morphology and composition of the catalyst support that should allow optimal distribution and stabilization of the catalyst nanoparticles, anchorage of functional groups, good electronic conductivity, facile mass transport of reactants and products as well as high corrosion stability under oxidizing conditions [3,4]. Commonly, most of low and middle temperature fuel cells rely on low-cost mass-produced carbon black materials with predominant microporous domains (< 2 nm) that are mostly not or partially accessible for reactants, exposed to corrosion process and consequently severely affect catalyst performance and durability.

One of the main obstacles for widespread commercialization of proton exchange membrane fuel cells (PEMFC) is related to its insufficient long-term stability especially at high current densities [5]. Meanwhile five main mechanisms have been identified as causes for electrochemically active surface area (ECSA) degradation of Pt: (i) Ostwald ripening-based coarsening (dissolution of small metal particles and precipitation onto larger ones); (ii) migration on carbon support and coalescence; (iii) detachment, (iv) dissolution and precipitation in ionomer phase and (v) carbon corrosion. Pt dissolution mechanism is strongly influence by particle size and is governed by so-called Gibbs-Thomson effect [6,7]. Smaller particles have a higher surface energy, which causes a shift in the equilibrium dissolution potential to less positive values. Thus an exponential increase in dissolution rate with decreasing particle size was suggested, so that particles of diameters smaller than 2 nm are expected to dissolve at orders of magnitude faster than particles with diameters of for instance 5 nm. This is in accordance with some results issued from former identical location transmission electron microscope (IL-TEM) studies [8]. Huge impact of carbon nature and morphology on catalyst longevity is therefore well-admitted but still not fully understood. We recently demonstrated that adequate nature of carbon with middle BET surface (50–100 m^2 g^{-1}) combined with graphitic domains can drastically improve catalyst longevity for oxygen reduction reaction/ oxygen evolution reaction (ORR/OER) in

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alkaline environment [9].

Because of its different micro textures and morphologies, carbon is still an attractive material for a large range of electrochemical applications [10]. Carbon as support material for nano disperse electrocatalyst should fulfill following criteria; (i) good electrical conductivity, (ii) suitable host for the catalyst particles and (iii) high corrosion stability under oxidizing conditions [3,4]. Proper choice of support material is determinant for performing and durable catalyst [11,12]. Ideally, carbon material should additionally possess predominantly mesoporous structure with large surface area, pore volume as well as narrow pore size distribution. The large surface area and 3D connected mono-dispersed mesospheres facilitates diffusion of the reactants, making them very attractive materials as fuel cell catalyst supports [13].

One discerns two types of mesoporous carbon: ordered (OMC) and disordered (DOMC) ones. OMCs are the most promising systems and therefore have been extensively studied as alternative catalyst support materials to micropore ones such as carbons black for fuel cells applications [14–16]. In particularly, graphitized carbon hollow spheres deserve unique features of good gas penetrability and optimal pore size distribution for nanoparticle confinement with improved activity for ORR and stability. The latter property was attributed to the presence of numerous graphitic domains [17]. Hayashi et al. [18] built an ideal triple-phase boundary inside the mesopores of carbon support in order to examine the electrochemical reactions at nanoscale. The effect of mesoporous carbons pore morphology on electrocatalytic activity of 20 wt% Pt was also studied [19] on OMC (CMK-3) and disordered wormhole mesoporous carbon (WMC). It was found that CMK-3 support provided more electrochemically active Pt sites and higher active surface area than WMC, leading to superior ORR activity and fuel cell performance. This enhanced catalytic activity was attributed to the highly ordered structure and good 3D interconnection of the nanospacings of carbon nanorods, resulting to higher catalyst utilization compared to WMCs. Lust et al. [20,21] studied activity of ordered micro-mesoporous tungsten and molybdenum carbide derived carbon (CDC) supported catalysts for ORR. Best results in terms of activity normalized to Pt mass amounted 27 A g^{-1} and was obtained with Pt–C(Mo_2C)800. Novel ordered hierarchical mesoporous/microporous carbon (OHMMC) derived from mesoporous titanium-carbide/carbon composites was prepared by synthesizing ordered mesoporous nanocrystalline titanium-carbide/carbon composites, followed by chlorination of titanium carbides and tested for supercapacitor applications [22].

Kim et al. [23] studied the durability of ordered mesoporous carbons OMC-supported (CMK-3, CMK-3G, and CMK-5) Pt catalysts in the potential range from 0.6 to 1.2 V at 50 mV s^{-1} for 2000 cycles. Highly graphitized CMK-3G was less prone to formation of surface oxygen functional groups during potential cycling compared to CMK-3 and CMK-5 (amorphous-carbon-like frameworks). They claimed that mass activity of the catalysts is nearly inversely proportional to micropore volume of the carbon supports. Grozovski et al. [24] measured about 80 mV less overpotential for ORR on microporous–mesoporous carbons-supported Pt (100) nanocubes compared to Pt(100) on Vulcan. Maiyalagan et al. [25] observed a threefold higher mass activity of 3D cubic OMC-supported (CMK-8) Pd (486 mA mg^{-1}) at 0.3 V for ORR in 0.5 M HCOOH + 0.5 M H_2SO_4 compared to that of Pt/C. By using a hard-template route, Galeano et al. [17,26] have developed mesoporous highly graphitized carbon hollow spheres with a specific surface area of about 1000 m^2 g^{-1} and average pore size distribution in the range of 3–4 nm that allow perfect Pt nanoparticles confinement and slow down degradation processes such as particle detachment and coalescence. Another interesting strategy aims at the development of catalyst-free catalysts. Popov and coworkers [27] synthesized N-doped ordered mesoporous carbon (CNx) via a nanocasting process by using polyacrylonitrile (PAN) as nitrogen and carbon precursors while mesoporous silica served as template. After a pyrolysis process in argon at 1000 °C, a current density of 0.6 A cm^{-2} at 0.5 V was obtained in a H_2/O_2 PEFC using 2 mg cm^{-2} catalyst loading.

Table 1
BET and average pore diameter values of the different carbons used in this work (data provided by manufacturer).

Product name	Description	Supplier	BET surface m^2 g^{-1}	Avg. pore size nm	Avg. particle size nm
Vulcan	Carbon black	Cabot	240	2	50
$HSAG_{300}$	High Surface Area Graphite	TIMCAL	250	–	15
OMC	Ordered Mesoporous Carbon	ACS Material®	1000	3.9-5.5	500-5000
GNP_{10}	Graphite Nano Particles	ACS Material®	660-720	–	10
GNP_{500}	Graphitized Nano Particles	Sigma Aldrich	100	6.4	50

This work aims at the study of highly active and corrosion-resistant Pt/C catalyst for the middle-temperature (120–150 °C) DMFC cathode. First results about preliminary screening of several as-prepared and commercial available carbon/graphite-supported 40 wt% Pt catalysts regarding their activity for ORR under rotating ring disk electrode (RRDE) and gas diffusion electrode (GDE) cell conditions as well as their stability under accelerated stress tests are presented.

2. Experimental

The commercial available carbon materials tested in this work were used as received and listed in Table 1 as follows: (1) carbon black (Vulcan XC-72R, Cabot); (2) High Surface Area Graphite ($HSAG_{300}$, Timcal); (3) Ordered Mesoporous Carbon (OMC, ACS Materials); (4) Graphite Nano Particles (GNP_{10}, ACS Materials); and (5) mesoporous Graphitized Nano Particles (GNP_{500}, Sigma Aldrich).

Pt/Carbon catalysts were prepared first by impregnating the carbon support with desired amount of hexachloroplatinic acid ($H_2PtCl_6.6H_2O$, Alfa Aesar) (99.99%) followed by a reductive process in 37 wt% formaldehyde stabilized with 10% methanol (Merck) at 80 °C for 1 h under reflux conditions. Reaction products were washed with ultrapure water (> 18.18 MΩ cm, ELGA Millipore), filtered through a 0.45 μm polycarbonate membrane (Sartorius) and finally dried in a vacuum oven (Thermo Scientific VT6025) at 80 °C and 50 mbar for 4 h. Nominal total metal loading on carbon supports were fixed to 40 wt.%. For comparison, commercial 40 wt.% Pt/C benchmark catalysts were purchased by QuinTech e.K. / Johnson Matthey (Pt/C_{JM}) and Heraeus GmbH (Pt/$C_{Heraeus}$).

Amount of the Pt loading on carbon support catalysts was estimated by thermo-gravimetric analysis (TGA) (NETZSCH STA 449 F3 Jupiter). Structural analysis of the catalysts was performed by X-ray diffractometer (XRD) (Bruker D8 Advance) equipped with Cu-K_{alpha} radiation (λ = 0.154 nm). Surface morphology and atomic/weight ratio of the catalysts were determined by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) (Philips XL 40), respectively.

Electrochemical investigations were performed with a 0.205 cm^2 rotating glassy carbon disk and Pt ring electrode (RRDE) (Pine Research Instrumentation). Catalyst ink suspension was prepared as reported in a previous work [28]. Briefly, 2 mg of catalyst powder was dispersed in 1 ml of water:isopropanol mixture (1:2) and ultrasonicated for 5 min. About 20 μl of 1–10 wt% Nafion® (Ion Power, Inc.) containing ink was transferred onto the glassy carbon electrode. A total catalyst loading of about 80 ± 10 μg_{Pt} cm^{-2} was maintained for all systems.

Steady-state cyclic voltammograms (CV) were recorded with a bipotentiostat (Pine Research Instrumentation WaveDriver 20). A Pt wire and a saturated calomel electrode (SCE) were employed as counter and