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Microstructure effects on the electrochemical corrosion of carbon materials and carbon-supported Pt catalysts

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ABSTRACT

The electrochemical corrosion behavior of a set of porous carbonaceous materials of interest as catalyst supports for polymer electrolyte membrane fuel cells was examined in 2 M H_2SO_4 at 80 °C at constant electrode potential of 1.2 V vs. RHE. Correlations have been observed between the specific rates of corrosion of carbon materials and carbon-supported Pt catalysts on the one hand and their substructural characteristics derived from X-ray diffraction analysis on the other hand. Carbon supports of the Sibunit family and catalytic filamentous carbons possess lower specific (i.e., surface area normalized) corrosion currents compared to conventional furnace black Vulcan XC-72 and better stabilize Pt nanoparticles.

1. Introduction

The durability of polymer electrolyte membrane fuel cells (PEMFCs) has recently been recognized as a major barrier to their commercialization for stationary and transportation power applications [1–3]. Several processes contribute to the loss of performance of PEMFCs (see reviews [4,5] and references therein), among these corrosion of platinum and carbon support.

The crucial role of corrosion of carbon materials was first recognized during the development of phosphoric acid fuel cell (PAFC) technology. Thermodynamically carbon is unstable at potentials of PAFC or PEMFC cathode operation ($E^0_{CO_2/C} = 0.207$ V vs. SHE at 298 K [6]). In 1970s–1980s, the electrochemical corrosion of various carbon materials was extensively studied in H_3PO_4 medium under PAFC-relevant conditions. An outstanding review of these publications is provided in Kinoshita's treatise [6]. Kinoshita and Bett [7] conjectured that electrochemical carbon corrosion comprises contributions of two concurrently occurring electrochemical reactions: (i) formation of surface oxides and (ii) evolution of CO_2. While the rates of both processes decay with time, the faradic efficiency of the CO_2 evolution increases [7]. The rate of corrosion was found to increase with the electrode potential, temperature, water concentration [6], and decrease with the concentration of phosphoric [8] or sulfuric acid [9].

Progress in the development of PEMFCs has recently boosted interest in the carbon corrosion in carbon–Nafion® composites either in an operating fuel cell or under conditions relevant to the PEMFC operation [10–16]. When performed below 90 °C in the potential interval of the PEMFC cathode, the corrosion tests must be run for hundreds or even thousand hours in order to detect measurable degradation phenomena. Hence, model accelerated corrosion studies are often performed in aqueous H_2SO_4 solutions at potentials above 1.1 V vs. RHE.

It has long been recognized that morphology, structure and surface properties of carbon materials strongly affect their propensity to the electrochemical corrosion. Studies performed in H_3PO_4 medium have revealed that mass normalized corrosion currents increase with the BET surface area S_{BET} [17] and the interlayer spacing d_{002} of quasi-graphitic crystallites [17–19]. Various structural defects on the surface and in the bulk of carbon materials are considered to be responsible for their degradation in aggressive media. Most prone to corrosion is the so-called amorphous or disordered carbon which is rich in defects, and is in the first place attacked either by the gas-phase or by the electrochemical oxidation. Amorphous carbon can readily react with oxygen at ambient conditions to form surface oxygen-containing groups.

Giordano and co-workers [18,20] examined the electrocorrosion of a set of carbon blacks with S_{BET} ranging from 42 to

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Table 1
Textural and substructural characteristics of carbon materials.

Carbon material	Surface area/$m^2\,g^{-1}$	Pore volume/$cm^3\,g^{-1}$		Mean pore diameter/nm	Mean crystallite size/nm		Interlayer spacing/nm	Intensities ratio
	S_{BET}	V_{Σ}	V_{μ}	D	L_a	L_c	d_{002}	I_{002}/I_{10}
CNF-I herringbone	80	0.276	0.0011	13.8	5.8	6.0	0.342	5.26
CNF-II platelet	182	0.465	0.0035	10.2	5.0	7.4	0.340	5.26
CNF-III nanotube	164	–	–	–	5.4	6.7	0.341	8.33
Sibunit 19P	72	0.154	0.0041	8.5	5.4	3.4	0.349	4.55
Sibunit 150P	198	0.145	0.081	2.2	4.5	3.0	0.353	5.26
Sibunit 20P	292	0.416	–	5.7	3.8	4.2	0.349	4.31
Sibunit 619P	415	0.593	–	5.7	4.0	3.5	0.352	6.00
Vulcan XC-72	222	0.428	0.026	7.7	3.9	2.1	0.356	4.17
P-277	219	0.431	0.042	7.9	1.9	1.7	0.362	5.20
P-267	228	0.595	0.045	10.5	1.2	1.4	0.361	3.60

$1475\,m^2\,g^{-1}$ in H_3PO_4 at 170 °C and conjectured that specific corrosion currents measured after 100 min of oxidation under potentiostatic conditions at 1 V vs. RHE increase with the initial surface concentration of the oxygen-containing groups. They hypothesized that the surface oxygen-containing complexes are the sites of the primary attack in the electrooxidation process. Similar conclusion has recently been achieved by Colmenares et al. [21]. This conclusion should however be reconciled with the known increase of the surface concentration of the oxygen-containing groups along with the decay of corrosion currents in time [7]. It is worth mentioning that the concentration of the surface oxygen functionalities is interrelated with the fraction of amorphous carbon and other imperfections.

Recent studies performed in aqueous H_2SO_4 under conditions relevant to PEMFCs also give evidence of the influence of microstructure of carbon materials on their corrosion behavior. Colmenares et al. [21] using differential electrochemical mass spectroscopy confirmed higher stability of graphitized carbons to corrosion, while Shao et al. [22], Wang et al. [23] and Li and Xing [24] established higher corrosion resistance of carbon nanotubes compared to conventional carbon black Vulcan XC-72.

Recently proprietary carbons of the Sibunit family obtained by pyrolysis of hydrocarbons [25] have attracted attention as promising support materials for the cathode of a PEMFC and the anode of a DMFC [26–28].

The aim of the present work is to compare corrosion tolerance of the Sibunit carbons and Sibunit supported Pt catalysts with that of furnace blacks and carbon filaments, and analyze the relationships between the microstructure of carbon materials and their corrosion behavior. Powder diffraction, high resolution transmission electron microscopy, and low temperature N_2 adsorption studies are employed to access the microstructure of carbon materials in this work. Corrosion is studied in aqueous 2 M H_2SO_4 under conditions relevant to PEMFC application: 80 °C and $E = 1.2$ V vs. RHE. While the cathode potential does not reach this value under "normal" cell operation, it is achieved during shut down/start up procedures, strongly accelerating degradation of the catalytic layers.

2. Experimental

2.1. Materials preparation and characterization

Carbon materials studied in this work fall into three groups: (i) commercial furnace blacks Vulcan XC-72 (Cabot), P-277 and P-267 (Omsk Carbon Black Plant, Russia); (ii) proprietary carbon supports of the Sibunit family obtained via hydrocarbon pyrolysis and subsequent activation [25,29] (Institute of Problems of Hydrocarbon Processing, Omsk, Russia); and (iii) experimental batches of catalytic nanofilaments (CNFs) with "herringbone" (CNF-I), "platelet" (CNF-II) and "nanotube" structure (CNF-III) [29] (Boreskov Institute of Catalysis, Novosibirsk, Russia)

Textural characteristics of carbons were obtained from the data on the nitrogen adsorption measured at 77 K with an automatic volumetric device ASAP 2400 (Micrometritics). The samples were pre-treated at 573 K to residual pressure of ca. 10^{-3} Torr. The adsorption isotherms were then used to calculate values of the BET specific surface area S_{BET} (in the range $P/P_0 = 0.05–0.2$) and total pore volume V_{Σ} (at $P/P_0 = 0.98$). Here P_0 is the saturation pressure. The volume of micropores V_{μ} accessible to nitrogen at 77 K was determined using the comparative method of Karnaukhov et al. [30]. The values of the mean pore diameter D were calculated on the basis of the BET model as $D = 4V/S$.

Substructural parameters of the carbon materials were calculated from their X-ray diffraction (XRD) patterns obtained using X-ray diffractometer (Siemens, Cu K_{α} radiation). These include the average in-plane diameter L_a, the average size of quasi-graphitic domains in the direction perpendicular to graphene layers L_c, the average interlayer spacing d_{002} within these domains, and the ratio I_{002}/I_{10} between the integral intensities of 0 0 2 and 1 0 diffraction lines. Note that I_{002} and I_{10} are related to the fraction of sp^2 carbon atoms comprised in three-dimensionally ordered quasi-graphitic crystallites, and in two-dimensional graphene sheets, respectively. L_c and L_a were estimated from Scherrer equation using the half-width values of the 0 0 2 and 1 0 diffraction reflexes correspondingly, d_{002} was calculated from the position of 0 0 2 line

Table 2
Characteristics of carbon-supported Pt catalysts.

Sample	Pt loading per carbon surface area/$mg\,m^{-2}$	Pt dispersion D	Particle size from CO chemisorption/nm	Particle size from TEM/nm	
				$\bar{d}_{TEM} = \sum_i d_i/N$	$\bar{d}_{S,TEM} = \sum_i d_i^3/\sum_i d_i^2$
10%Pt/Sibunit 19P	1.54	0.29	3.7	2.4	4.5
20%Pt/Sibunit 150P	1.26	0.29	3.7	–	–
40%Pt/Sibunit 619P	1.61	0.18	5.9	2.7	3.5
20%Pt/Vulcan XC-72	1.13	0.31	3.4	2.6	4.9
20%Pt/P277	1.14	0.31	3.4	3.5	4.1
20%Pt/P267	1.10	0.34	3.1	–	–