



Further insights into the role of carbon in manganese oxide/carbon composites in the oxygen reduction reaction in alkaline media



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ABSTRACT

Manganese oxides are known as active catalysts for the oxygen reduction reaction (ORR) in alkaline media. Being poor electronic conductors, for electrochemical applications, most of Mn oxides are either mixed with or supported on carbon materials, which impart electronic conductivity to the composite electrodes. A number of recent publications reported an immense influence of carbon materials on the electrocatalytic activity of transition metal oxides in the ORR. To better understand the role of carbon, in this work we utilize a wide variety of carbon materials and investigate the ORR on Mn₂O₃/carbon composites combining experiment with kinetic modeling. Such an approach allows us to discriminate the contribution of carbon in the ORR activity of composites, underscoring its positive role in improving the oxide utilization, and acting as the ORR co-catalyst, but also its negative role in competing for the adsorption of O₂. By juxtaposing the electrocatalytic activity with the structural and morphological characteristics carbon materials, we propose some rules of thumb for choosing carbons necessary for creating efficient oxide/carbon ORR electrocatalysts.

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1. Introduction

Manganese oxides have been widely studied in the past as promising catalysts for the electrochemical oxygen reduction reaction (ORR) in alkaline media in view of their potential applications for fuel cells and metal-air batteries [1–7]. Considering low electronic conductivity of many of transition metal oxides, including manganese, for practical applications they are usually utilized as oxide/carbon composites, which can be prepared either by mixing of the two components [8–12], or by synthesizing hybrid materials [13–20]. Numerous publications demonstrated an important influence of carbon in the oxide/carbon composites on the ORR activity and proposed possible reasons for the activity increase [9–12]. Poux et al. [9] suggested that carbon in the oxide/carbon composites plays a dual role. On the one hand, it improves the conductivity of the catalytic layer, leading to the increase in the number of active sites on the transition metal oxide surface

available for electrocatalysis. On the other hand, it acts as co-catalyst, accelerating the oxygen reduction to hydrogen peroxide, which then further reacts on the surface of oxide, resulting in an overall apparent 4e⁻ ORR. A kinetic model was put forward allowing to explain the ORR on oxide/carbon composites semi-quantitatively [21,22]. Some authors proposed that in addition, carbon may affect the oxidation state of transition metal [23] and/or form covalent bonds with the transition metal oxide particles [17,24]. It has been demonstrated that not only the amount [9–11] but also the type of carbon material [12,25] in the oxide/carbon composite affects the ORR activity, which can be enhanced by order(s) of magnitude compared to the oxide alone. Thus, detailed understanding of the role of carbon in the ORR on oxide/carbon composites is not only interesting from the fundamental point of view, but also essential for the development of potent materials for practical applications.

In this work we investigate the catalytic activity of composites of Mn₂O₃ oxide, an exceptionally active ORR catalyst [26,27], with various carbon materials. In order to bridge the ORR activity of oxide/carbon composites with the structure and morphology of carbons, we have chosen a range of carbon materials, widely

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Table 1
Characteristics of carbon materials.

Carbon material	Abbreviation	S_{BET} , $\text{m}^2 \text{g}^{-1}$	S_{BJH} , $\text{m}^2 \text{g}^{-1}$	D_{BJH} , nm	Contact angle, °		C_{BET} , $\mu\text{F cm}^{-2}$	C_{BJH} , $\mu\text{F cm}^{-2}$	θ basal planes	L_a , nm	L_c , nm	d_{002} , nm	Micropore area, $\text{m}^2 \text{g}^{-1}$
					Carbon	$\text{Mn}_2\text{O}_3/\text{C}$ composite							
Sibunit 176	S-176	6	4	16.0	60	38	238	354	–	0.23	0.24	0.0355	~0
Sibunit 152	S-152	65	52	27.5	50	31	22	27	0.62	0.27	0.25	0.0355	~0
Sibunit 1519	S-1519	272	117	11.1	56	34	9.3	22	0.71	0.28	0.33	0.0353	~0
Acetylene black	AB	64	47	16.1	140	115	12	16	0.79	0.29	0.30	0.0352	~0
Vulcan XC-72	VU	221	50	21.9	85	0	8.4	37	0.48	0.23	0.19	0.0364	112.6
Ketjenblack 300J	KB	858	262	11.5	58	46	2.4	7.8	0.91	0.23	0.14	0.0364	~0
Multiwall carbon nanotubes	CNT	98	67	14.2	150	135	7.8	11	0.86	0.20	0.66	0.0344	~0
CFC-1	CFC	175	66	13.1	0	0	12	31	0.57	0.36	0.47	0.0345	29.7

differing in their specific surface areas, average pore size, surface properties and microstructure.

2. Experimental

2.1. Materials

Mn_2O_3 was prepared from MnOOH by heating the latter in air at 600°C for 2 h. The MnOOH sample was prepared according to the procedure described in Ref. [28]. The BET surface area of Mn_2O_3 was $22 \text{ m}^2 \text{g}^{-1}$.

Carbon materials with various morphologies and microstructures were used in this work (Table 1). Shawinigan Acetylene Black (AB), Vulcan XC-72 (VU) and Ketjenblack 300J (KB) were purchased from ChevronPhillips, Cabot and AkzoNobel, correspondingly. Catalytic filamentous carbon (CFC) was obtained by catalytic decomposition of CH_4 over a Ni-containing catalyst [29]. Multiwall Carbon Nanotubes (CNTs) were produced by catalytic ethylene decomposition over Fe–Co catalysts as described in Ref. [30] then washed with HCl to remove the catalyst, and subjected to mechanochemical treatment in a planetary ball mill Pulverisette 6 (Fritsch) for 4 hours at 400 rpm. For more details on the CNT sample preparation and treatment the reader is referred to Ref. [31]. Carbons of the Sibunit family (Sibunit-176, Sibunit-152 and Sibunit-1519) are proprietary materials [32] obtained by pyrolysis of hydrocarbons onto a carbon black template in the temperature range from 1120 to 1220 K followed by steam activation in a fluidized bed at 973 to 1120 K [33,34]. Sibunit carbons utilized in this work differ in the degree of the steam activation. Thus, longer activation of Sibunit-1519 compared to Sibunit-152 accounts for the higher S_{BET} of the former, while Sibunit-176 was not subject to any activation procedure. Obviously, in order to serve as conductive binders, carbon materials must possess high electrical conductivity. All carbon materials investigated in this work are known to be good electron conductors [34].

2.2. Sample characterization

For Mn_2O_3 the X-ray powder diffraction (XRD) characterization of phase composition was performed with a Huber G670 Image plate Guinier diffractometer ($\text{CuK}\alpha_1$ radiation, curved Ge monochromator, image plate detector). Substructural characteristics of the carbon materials were derived from their X-ray diffractograms recorded with a DRON-3 M X-ray diffractometer (monochromatic $\text{CuK}\alpha$ irradiation). The sizes of the domains of X-ray coherent scattering, L_a and L_c , were estimated using Scherrer equation subject to the instrumental width of the diffraction reflexes and their broadening caused by the α_2 component of the $\text{CuK}\alpha$ doublet. The interlayer spacing, d_{002} , in the domains was calculated from the Bragg equation.

N_2 physisorption isotherms were measured with ASAP 2010 analyzer (Micromeritics, USA) and used to determine the specific surface area by multiple-point Brunauer-Emmett-Teller (BET) approach (S_{BET}). Surface area (S_{BJH}) and average size (D_{BJH}) of the pores with the size ranging from 1.7 nm to 300 nm was determined using the BJH method from the adsorption branch of the isotherm. The micropore area and volume were obtained using the t-plot method of Lippens and de Boer for treatment of the adsorption data. The respective values are given in Table 1. Pore size distributions are plotted in Fig. S1.

Transmission electron microscopy (TEM) images were obtained with JEOL 2100F microscope operated at 200 kV. Fig. 1 shows high resolution TEM images of selected carbon materials demonstrating their different morphologies (for low resolution TEM images the reader is referred to Fig. S2). TEM images for selected oxide/carbon composites are shown in Fig. S3. AB and VU consist of the so-called primary particles with ca. 40 and 20–30 nm diameter, correspondingly. However, one may notice that graphene layers are more ordered on the surface of AB globules, while for VU they are distorted, exposing significant number of edge and defect sites to the surface. Activated Sibunit carbons possess very different egg-shell morphology, whereby the holes inside the shells are created by gasification of the carbon black template as one may notice from TEM images of S-152 in Figs. S2 and S3b.¹ The CFC sample clearly shows a herring-bone structure with the edge planes exposed to the surface of carbon filaments. KB demonstrates a highly porous morphology, and consists of a few graphene layer thick “ribbons”, presumably exposing basal planes to the surface.

X-Ray Photoelectron Spectroscopy (XPS) measurements were performed in an ultra-high vacuum chamber (pressure $<5 \times 10^{-6}$ Pa) equipped with a VG Microtech Clam2 electron analyzer and a dual anode (Al and Mg $\text{K}\alpha$) X-ray source. The C 1s spectra were recorded using excitation photon energy of 1486.6 eV, which corresponds to an approximate analysis depth (estimated as a mean-free path multiplied by 3) of 14 nm. Following Ref. [35], the C 1s peak was fit with four singlets, corresponding to carbon of the C–C network (BE = 284.4 eV), C–O (BE = 286.0 eV) C=O (BE = 288.5 eV) and C–OO[–] (BE = 290.4 eV) functionalities.

Scanning electron microscopy (SEM) measurements and EDX mapping were performed with Zeiss ULTRA plus with charge compensation at 1 kV.

Contact angle measurements were performed at room temperature by sessile drop technique with the accuracy ± 1 degree. The macroscopic advancing contact angles were measured using horizontal microscope with a goniometer (magnification 25). Contact angles for carbons and oxide/carbon composites are listed

¹ “Bulky” morphology of carbon aggregates in Sibunit carbons is responsible for the lower quality of TEM images compared to other carbon materials (see Fig. S2).

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