Article

Elucidation of oxygen reduction reaction pathway on carbon-supported manganese oxides

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ARTICLE INFO

ABSTRACT

The oxygen reduction reaction (ORR) is a complex process. This is particularly the case for carbon-supported electrocatalysts in alkaline electrolytes, because carbon can catalyze the ORR via a two-electron transfer to generate hydroperoxide (HO_2^-), which subsequently undergoes either chemical decomposition to generate O_2 and OH^- (HODR) or electrochemical reduction to OH^- (HORR). In this study, we elucidated the ORR pathway on a series of carbon-supported manganese oxides, which have been extensively studied as electrocatalysts in alkaline electrolytes. A comparison of the turnover frequencies of the HODR and HORR showed that although an apparent four-electron transfer process was identified when the HO_2^- yield was measured using the rotating ring disk electrode technique, the real ORR pathway involved a two-electron transfer process to generate HO_2^-, with subsequent chemical decomposition of HO_2^-. These results will help us to understand the intrinsic catalytic behavior of carbon-supported transition-metal oxides for the ORR in alkaline electrolytes.
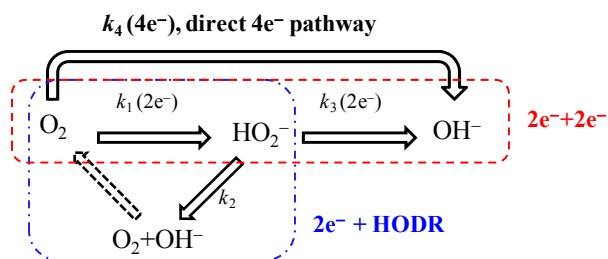
1. Introduction

The oxygen reduction reaction (ORR) is very important because it is the cathodic reaction in fuel cells and metal–air batteries. Pt-based materials are extensively used as ORR catalysts under acidic conditions, but under alkaline conditions, a wide range of non-noble metals and their oxides are stable and active for practical applications [1–3]. An understanding of the ORR pathway on a catalyst surface is critical in both fundamental and practical terms. Although the ORR pathway on a smooth catalyst surface can be easily studied using the rotating ring disk electrode (RRDE) technique, for a carbon-based prac-

tical porous electrode, the ORR pathway is complex because the considerable amount of intermediate HO_2^- generated at the carbon surface can be readsorbed for further reactions. Specifically, hydroperoxide species have three possible subsequent pathways, as shown in Scheme 1, i.e., (1) diffusion directly into the electrolyte as a product, (2) further electrochemical reduction to form OH^-, and (3) chemical decomposition to produce O_2 and OH^-. Unlike case (1), cases (2) and (3) are apparent four-electron processes, although only case (2) is a real four-electron process. Our previous study of carbon-supported cobalt oxides [4,5] clearly showed that although the apparent electron transfer number was close to four in a large potential

k_4 (4e⁻), direct 4e⁻ pathway

Scheme 1. Various possible mechanisms for O_2 reduction in alkaline solution.

window, different electrochemical reactions occurred depending on the electrode potential, i.e., a two-electron transfer process followed by chemical decomposition of hydroperoxide at low overpotentials, but two-electron transfer followed by further electrochemical reduction of hydroperoxide, namely a serial four-electron transfer process, at high overpotentials.

Other promising transition-metal oxides, e.g., manganese oxides, are also worth investigating to help us to understand catalysis of the ORR by transition-metal oxides. Previously, it was concluded that a two-electron transfer process with subsequent chemical decomposition of hydroperoxide occurred on a manganese oxide surface [6,7]. However, there is still a lack of experimental evidence to support this deduction. In this paper, continuing our previous study on the effects of manganese valences in manganese oxides on ORR activity [8], we aim to elucidate the ORR pathway on carbon-supported manganese oxides. The manganese oxide samples used in this study are the same as those used in our previous study [8]; therefore, the preparation procedures will not be described again. First, we calculated the electron transfer number of the ORR according to the Koutecky–Levich equation by measuring the ORR polarization curves via the rotating disk electrode (RDE) technique. We then distinguished between direct and indirect four-electron transfer processes by detecting the HO_2^- yields at manganese oxides of different catalyst thicknesses via the RRDE technique. Finally, we determined the main reactions in peroxide chemical decomposition (HODR) and electrochemical reduction (HORR) by measuring the turnover frequencies (TOFs) of the two reactions.

2. Experimental

2.1. Experimental setup

A traditional three-electrode system was used for RDE and RRDE measurements. The RDE (Φ 5 mm, glassy carbon (GC)] measurements were performed using a CHI 760D electrochemical workstation. The RRDE measurements were performed using a Bi-potentiostat (Pine Instruments). GC covered by a porous catalyst film was used as the working electrode, and Pt wire and a Hg/HgO electrode (MMO, in 1 mol/L NaOH, 0.93 V vs reversible hydrogen electrode after calibration) served as the counter and reference electrodes, respectively. The potential of the Pt ring electrode was kept at 0.2 V vs the MMO during the RRDE tests.

2.2. Working electrode preparation

The preparation of the working electrode has been described in detail in the literature [9]. Briefly, catalyst powder (3 mg) was dispersed in ethanol (2 mL). Carbon powder (2 mg; Vulcan XC-72, Cabot Corp.) was added to increase the conductivity, and 5 wt% Nafion solution (50 μL; DuPont) was added as a binder. The mixture was ultrasonicated to form a well-dispersed ink. A certain amount of the ink was pipetted onto the GC electrode and then the solvent was evaporated at room temperature to form a catalyst thin film. All the MnO_x catalyst samples were fresh, without any electrochemical pretreatment.

2.3. Determination of ORR and HORR polarization curves

The ORR and HORR polarization curves were recorded in O_2-saturated 1 mol/L NaOH solution and N_2-saturated 1 mol/L NaOH containing 0.85 mmol/L H_2O_2 solution, respectively, at a scanning rate of 10 mV/s.

2.4. TOF measurements (HODR)

GC covered with a Pt/C catalyst was used as a probe to detect the changes with time in the H_2O_2 concentration in the electrolyte after adding MnO_x as the HODR catalyst. The measurements were also carried out in a three-electrode system [10]. The preparation procedure for the thin-film electrode with Pt/C as the electrocatalyst was the same as that described above for the MnO_x electrode. After electrochemically cleaning the electrode surface at a scanning rate of 100 mV/s in 1 mol/L NaOH, the ORR limiting current ($i_{lim,ORR}$) was recorded by holding the electrode potential at −0.5 V for 10 s, with the electrode rotating at a speed of 1600 rpm. Then H_2O_2 (30%) was added to the electrolyte to ensure a concentration of 0.85 mmol/L (the same concentration as that of O_2 in the O_2-saturated 1 mol/L NaOH solution) [11]. Then MnO_x (300 μg) dispersed in water (1 mL) was quickly added to the H_2O_2-containing electrolyte under magnetic stirring to ensure good contact of the MnO_x catalyst with H_2O_2. The Pt electrode was held at −0.5 V for 10 s to collect the current (i_{lim}) at intervals. The concentration of residual HO_2^- in the electrolyte could be calculated according to the current difference on the Pt electrode ($i_{lim,HORR} = i_{lim} - i_{lim,ORR}$). The measurements continued for only 10 s at each interval and then the Pt electrode was rapidly removed from the electrolyte after the tests, therefore it was assumed that no extra HO_2^- decomposed at the Pt surface.

3. Results and discussion

3.1. Measurement of ORR electron transfer numbers of carbon-supported manganese oxide electrocatalysts

The ORR polarization curves of the carbon-supported manganese oxide electrocatalysts were measured in O_2-saturated 1 mol/L NaOH electrolyte; the results are shown in Fig. 1. The ORR onset potentials of the four carbon-supported MnO_x catalysts with different manganese valences, i.e., $MnOOH/Mn(OH)_4$,