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The influence of KOH concentration, oxygen partial pressure and temperature on the oxygen reduction reaction at Pt electrodes

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ABSTRACT

In this paper, cyclic voltammetry (CV), linear sweep voltammetry (LSV) and rotating ring-disk electrode (RRDE) techniques were employed to investigate the influence of alkali concentration, oxygen partial pressure, and temperature on oxygen reduction reaction (ORR) at Pt electrodes in KOH solutions. It was found that as the KOH concentration increases, the ORR kinetics is greatly inhibited, and the ORR pathway gradually shifts from 4 electrons transfer reaction by directly forming OH^- to 2 electrons transfer reaction by forming HO_2^-. The intermediate species were detected by electrogenerated chemiluminescence and ultraviolet–visible spectrophotometer to confirm the alkali concentration-dependent ORR pathway. In addition, the ORR kinetics was found to be significantly improved by the increasing oxygen partial pressure due to the corresponding increase of oxygen solubility. However, the temperature exhibits dual effects toward ORR and the optimal temperature for the ORR was obtained in given alkaline solutions. The activation energy of ORR was calculated based on the RRDE data.

1. Introduction

Oxygen reduction reaction (ORR) is of great interest due to its wide application in fuel cells [1–4], biological processes [5] and other fields [6,7], which has been extensively studied in the previous research by both experimental and theoretical means [8–12]. Considerable molecular level analysis on the ORR mechanism as well as factors which affect the ORR kinetics have been achieved [13–15]. Different electrocatalysts have been reported to be able to catalyze the ORR in different ways. Structure–activity relationships have been derived for catalysts composed of either bulk single metals [16,17], or bimetallic alloys [14,15]. ORR mainly proceeds via a 4-electron pathway on Ag and Pt electrode [18,19], while 2-electron and 1-electron processes occur on the glassy carbon electrode [20]. Apart from the electrode materials, ORR kinetics has been found to be very sensitive to the electrolyte [21–23]. Recently, further research efforts have been attempted on the alkaline fuel cells [2,24,25] owing to its high electrical efficiency and operation flexibility. Its electrical efficiency can achieve 60% in moderate condition as compared to 25–58% for the polymer electrode membrane fuel cell (PEMFC) and 35–43% for the solid oxide fuel cell (SOFC), respectively [26]. This is due to its excellent ORR kinetics compared to the acidic condition in other fuel cells and also the high ion conductivity by using high OH^- concentration [26].

Researchers have examined the effect of alkali concentration [27,28] on the kinetics and pathway of the ORR. It was found out that the ORR process will be greatly inhibited with increase in alkali concentration, and thereby the reaction mechanism changes correspondingly. Reeve [29] investigated the effect of the minority additives on the ORR kinetics in various concentration of alkali carbonate electrolytes, and attributed the difference in ORR kinetics to the change of oxygen solubility and CO_2 diffusion. Further study suggested that increasing oxygen pressure and media temperature were expected to have a significant effect on the concentration and diffusion coefficient of reactants, which was beneficial for further understanding the ORR mechanism in alkaline media [23,26]. Peroxide species was generally recognized as one of the most probable intermediates during ORR [30] in alkaline media, which was further confirmed by Kattel and Wang [31] using DFT calculations in their recent study. However, a consensus on the understanding with respect to the ORR pathway has not been reached so far, as evidenced by deviations between the experimental results. Recently, Yang et al. [32] suggested that the ORR kinetics was

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determined by the kinetics for O_2^- decomposition to OH_{ads}, which varied with the pH. While Mohanraju and Cindrella [33] calculated the kinetics parameters such as mass and specific activities from the Tafel slope of the ORR using pure Pt electrode, and their results indicated a four electron transfer reaction mechanism with the first electron transfer as the rate determining step. Peng et al. [34] suggested that the ORR pathway was transformed from a two-electron reduction by forming peroxide in dilute solutions to a one-electron reduction by forming superoxide in concentrated solutions. While using Pt–N–C electrode, Gao et al. [35] proposed a dominating four-electron oxygen reduction pathway in alkaline solutions.

Besides, most of the ORR studies in alkaline media were carried out in dilute solutions (under 6 M) [27], and reports related to the ORR in highly concentrated alkaline medium are limited [23,36,37]. In view of the foregoing, the influence of alkali concentration, temperature and oxygen partial pressure on ORR in concentrated KOH solutions were systematically examined using cyclic voltammetry (CV), linear sweep voltammetry (LSV), and rotating ring-disk electrode (RRDE) techniques. Especially, the reaction intermediates were detected using fluorescent probe and ultraviolet–visible spectrophotometer to clarify the ORR pathway. The results are discussed to provide more information to understand the ORR mechanism in alkaline solutions.

2. Experimental

2.1. Materials and solutions

The reagents, including H_2O_2 and $K_3Fe(CN)_6$ used in the electrochemical experiments were of ACS reagent grade (Alfa aesar). Fluorescent probe 2′,7′-Dichlorodihydrofluorescein diacetate (H_2DCFDA) and the KOH stock solution (45% mass fraction, HPLC grade, total impurities $K_2CO_3 \leqslant 0.3\%$ mass fraction) were from Sigma Aldrich. All the solutions were prepared using Millipore Milli-Q water (18 MΩ cm) in a nitrogen-filled glove box to minimize contamination by CO_2 [38,39]. The solutions, saturated with high purity N_2 and O_2 (99.999% by volume, Beijing Qianxi Gas), were used as blank and working solutions, respectively.

2.2. Instrument and methods

The CV and LSV experiments were conducted in a self-designed Teflon electrochemical cell with 5 holes on the cover, of which one is for gas passageway, one is for thermocouple, and the others are for the three electrodes. The cell was well sealed with operating pressure of 0.4 MPa. The RRDE and chemiluminescence experiments were performed in a Teflon container with four necks.

All experiments were performed using an electrochemical workstation (CHI760E). The cell was heated using a HZ-9212S type thermostatic shaking water bath with a precision of 0.1 K. The working electrode, counter electrode and reference electrode are respectively Pt wire, Pt film and saturated Ag/AgCl electrode. A Pine Instrument's MSR rotator was used to control the Pine's Model E6 series ring-disk electrode. The diameter of the Pt disk electrode is 6 mm with an effective area of 0.285 cm^2, which was determined using the reduction curves of hexacyanoferrate(III) in 1 M KNO_3 solutions [40]. The inside and outside diameters of the Pt ring electrode are 7.5 mm and 9 mm, respectively. The collection efficiency in the RRDE experiments is 0.388.

The Pt wire and Pt ring-disk electrodes were polished with metallographic sandpaper (2000 mesh), followed by alumina powders (0.5 μm) to achieve a mirror smooth surface. Prior to each experiment, the electrodes were repeatedly rinsed and cleaned using deionized water in the ultrasonic cleaner to obtain a contamination free electrode surface. After that, the working electrodes were electrochemically pretreated via cyclic sweeping between the onset potential of hydrogen and oxygen evolution reactions in corresponding supporting electrolyte solutions till reproducible and well-defined cyclic voltammetry curves were obtained. The potential was ended at onset of hydrogen evolution. All the CV and LSV curves in this study were obtained following the same scan direction as described above (anodic scan followed by cathodic scan). Similarly, for the RRDE experiments the ring and disk electrodes were activated before recording to improve the reliability of the quantitative detection of peroxides. The applied potential range for current–potential curves of ORR is from 0.3 V to −0.45 V. The oxidation ring potential was set to be 0.6 V to detect peroxide. All the potentials reported are versus the standard hydrogen electrode (SHE) for consistency. The electrogenerated chemiluminescence experiments were conducted in dark environment in order to avoid oxidation by light stimulation. Prior multi-sweep cyclic voltammetry or potentiostatic sweep, the same dosage of fluorescent probe was added into the alkaline electrolytic solutions. After predetermined time of electrochemical reactions, the electrolytic solution was subjected to absorbance detection using ultraviolet–visible spectrometer.

3. Results and discussion

3.1. The influence of KOH concentration on ORR at Pt electrodes

Typical redox behavior of O_2 on Pt electrode in KOH solutions is shown in Fig. 1, and for comparison, CV curves obtained in N_2 saturated solutions are also presented. It is clearly that the presence of oxygen in the solution affects the redox behavior at Pt electrode surface. The reduction reaction occurs at approximately −0.1 V in 1 M KOH solutions (Fig. 1a), resulting in the significant increase in reduction current [23,41]. By comparing Fig. 1(a) and (b), it is found out that the alkali concentration has a significant impact on the oxygen reduction behavior, as indicated by inhabitation of ORR in concentrated alkaline solutions (Fig. 1b). In order to clearly elucidate the influence of solution concentration on ORR, the cathodic peak current (i_{pc}) of the ORR was calculated by subtracting the peak current in blank N_2 saturated solutions from the O_2 saturated solutions (the same for the following calculation of i_{pc} and RRDE data). The obtained cathodic peak current i_{pc} values are summarized in Table 1. The ORR kinetics (i_{pc}) is greatly frustrated with the increase in KOH solution concentration. Besides, the E_{pc} of ORR negatively shifts with increase in alkali concentration, which is due to the Nernst shift of the H_2O/H_2 and O_2/OH^- equilibrium potentials.

The influence of scan rates on the ORR peak current was studied. Fig. 2(a) presents the CV curves obtained at different scan rates (from 20 to 120 mV s^{-1}) in 1 M KOH solutions with saturated oxygen. As can be seen from Fig. 2(a), the cathodic peak potential (E_{pc}) of the ORR negatively shifts from −0.08 V at 20 mV s^{-1} to −0.11 V at 120 mV s^{-1}, which is in good agreement with the previous reports [23,37]. The plot of the peak current vs. $\upsilon^{0.5}$ is presented in Fig. 2(b). It can be seen that the peak current increases linearly with the $\upsilon^{0.5}$, indicating that the reaction proceeds as a theoretical diffusion-controlled process.

3.2. ORR pathway in concentrated KOH solutions

The ORR was also studied using RRDE technique to obtain the average electron transfer number (n) and other kinetic parameters. Fig. 3 shows three typical I–V curves for ORR occurred in 2.0, 4.0, and 8.0 M KOH solutions, respectively. Clearly, the ORR current proportionally increases with the potential decreasing from 0.1 V