Study of the Oxygen Reduction Process on Air Cathode*

OU Xiu-qin, LIANG Guang-chuan, XIE Fei, FAN Fei, LIU Shu-guang
(Institute of Power Source and Ecomaterials Science, Hebei University of Technology, Tianjin 300130, China)

Abstract: The volume of oxygen generated from the electrolysis bath made up of an air cathode and nickel anode is measured, and the proportion of the two courses, 2e and 4e path oxygen reduction process, can be distinguished quantitatively according to the relation between the gas generation per minute and the current. The results show that the 2e path reaction covers 74% on the air cathode using active carbon as electrocatalyst, while the 4e path reaction covers up to 100% when the percentage of the catalyst MnO_2 in the air catalyst layer of air electrode reaches 33%. This method can demonstrate the corresponding changes with time in the two kinds of oxygen reduction reaction.

Key words: oxygen reduction; air cathode; reaction process; catalyst
CLC number: O646.21 **Document code**: A **Article ID**: 0529-6579 (2005) S2-0091-04

Air cathode can be used as positive in fuel cell and metal-air battery[1-3], or used as cathode in electrochemical reactor, such as H_2O_2 generation by electrolyzing, electrochemical oxygen generator etc[4-7]. It can be instead of the hydrogen evolution electrode in Chlorine alkali industry and chlorate producing[8,9]. The electro catalyst of cathode is different in various application fields. The electro catalyst of the oxygen reduction in aqueous solution can be classified into two types: one type catalyst reacts following 2 electron path which forms peroxide, such as graphite and multiple carbon, aurum, hydrargyrum, nickel oxide, transition metal macrocyclic complex compounds such as CoTsPc, CoTMPP etc. The other type catalyst reacts mainly following 4 electrons path, such as platinum group of metals and alloy, silver, palladium metal, perovskite type oxide and niobpyrochlore type oxide, transition metal macrocyclic complex compound such as FeTsPc etc. The electron transfer number in the two reaction types and the electrode potential are both different.

The air electrode used in fuel cell and metal-air battery is made with carbon carrier on which sufficient amount of highly dispersed electrode catalysts are supported. The catalyst should let that the oxygen reduction react following 4 electrons process, in order to obtain high capacity and voltage to a battery[2]. Two electrons path reaction is expected in the electrolytic formation of inorganic peroxide. The author did not read any report about how to measure the proportion of each reaction. Moreover, the performance of air cathode is related not only to the activity and amount of the electrocatalyst, but also to the ratio of the electrode component in the mixture. The pore surface and structure of the cathode will change with the reaction time, and the change will influence the oxygen reduction process. The methods of linear polarization, rotating ring-disk electrode (RRDE), electrochemical impedance spectroscopy (EIS), etc, provide a plenty of information for study on the reaction dynamics of electrode. But these can't simulate the active state on-line of the cell and electrochemical reactor.

The paper introduced the method to calculate the ratio of the two types of oxygen reduction reaction in the air electrode on an electrolysis bath. The variation with time in the oxygen reduction reaction can be determined through measuring the volume oxygen generated and the current without considering the intermediate product and process.

1 Experimental

1.1 Electrolysis device

Fig. 1 shows a schematic drawing of electrolysis bath with an oxygen reduction cathode. It is composed of nickel sheet as the anode, asbestos paper as the membrane and air electrode as the cathode. The electrode area is 150 cm^2, and the electrolyte is 6 M KOH. Measuring the oxygen purity firstly, then measuring the gas generating amount while the oxygen purity is more than 99.8%. Calculating the oxygen output per ampere-minute according to the gas amount, time, current, water temperature and atmosphere pressure. The data can be used to illustrate the operation state of the air cathode.

* 收稿日期: 2005-07-10
基金项目: 天津市科技攻关计划资助项目(043102511)
作者简介: 欧秀芹 (1963 年生), 女, 高级工程师; E-mail: ouxiuqin@eyou.com

1.2 Test of oxygen purity

Test the oxygen purity according to the GB8982-1998 of medical oxygen.

1.3 Preparation of air electrode

Active carbon and acetylene black are mixed with MnO_2 catalyst. Stirring the mixture while disgregated with supersonic wave.

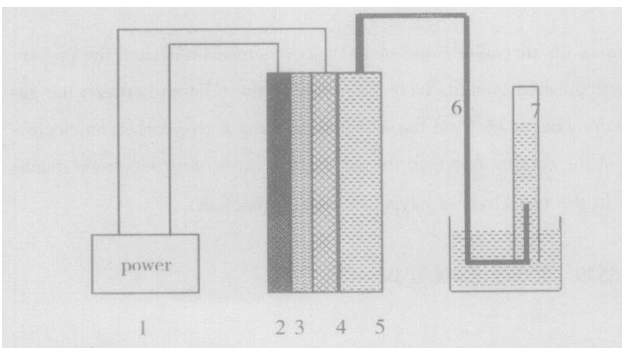

Fig 1 Schematic illustration of the oxygen evolution electrolysis cell

1. power 2. air cathode 3. asbestos membrane
4. nickel anode 5. electrolyte and oxygen chamber
6. pipe 7. measuring container

Polytetrafluoroethylene (PTFE) 60wt% emulsion is added to the mixture to form a dough which can be pressed into catalyst layer with a roller. Acetylene black, ethanol, PTFE emulsion are mixed with pore forming agent to obtain the waterproof layer by the same technique. The catalyst layer, current collector and the waterproof layer were stacked and pressed with a hydraulic press to be a cathode, which is to undergo thermal treatment in inert gas atmosphere to 350 ℃ for 1 h.

1.4 Test of polarization curve

The overpotential of the air electrode was evaluated on TD3691 potentialstat using a Lugin capillary tube placed close to the cathode and mercury-mercuric oxide electrode as a reference electrode, 6M KOH as the electrolyte, Nickel sheet as the auxiliary electrode. The area of working electrode is 1 cm^2, and the scanning rate is 10 mV/s. The electrode overpotential is measured with the Hg/HgO reference electrode.

2 Theory analysis and results

2.1 The relationship between final reaction process and oxygen evolution reaction

It is normally regarded that the oxygen reduction reaction on the air cathode takes place as the following two paths in aqueous alkaline solution[10]:

(1) 2 electrons process:

$$O_2 + H_2O + 2e \rightarrow OH^- + HO_2^- \quad (1)$$

$\varphi^0 = -0.065$ V

Following the electrochemical reduction reaction of HO_2^-:

$$HO_2^- + H_2O + 2e \rightarrow 3OH^- \quad (2)$$

$\varphi^0 = 0.867$ V

Or the chemical decomposition:

$$2HO_2^- \rightarrow 2HO^- + O_2 \quad (3)$$

(2) 4 electron path:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \quad (4)$$

$\varphi^0 = 0.401$ V

The sum of reaction Eqs (1) ~(3) is equal to reaction Eq (4). According to the standard electrode voltage, we know that the dynamic obstacle of reaction (4) is much more than that of reaction (1). The reaction (1) is unavoidable in aqueous alkaline solution for the electrode voltage of reaction (1) is very low. It is harmful to the increasing the electromotive potential. The catalyst added in electrode leads to the occurrence of reaction (4). Without regarding the interim process, the reaction can be mainly classified into 2 electrons and 4 electrons path in the cathode. Correspondingly, there are mainly two types of oxidation reactions as following in the anode.

$$OH^- + HO_2^- - 2e \rightarrow O_2 + H_2O \quad (5)$$

$$4OH^- - 4e \rightarrow O_2 + 2H_2O \quad (6)$$

FANG et al[5] have testified that the concentration of OH^- in the electrolyte didn't change when the electrolysis bath worked and there is not other discharge type in the anode. Corresponding to the two types of reduction reaction, there are two routes for the oxygen generating through the oxidation reaction at anode: one demands 2 mol electrons to generate 1 mol oxygen following reaction (5), the other demands 4 mol electrons to generate 1 mol oxygen following reaction (6). The generated oxygen amount can be determined by the ratio of reaction (5) and (6) in a definite time and current.

2.2 The relationship between oxygen generation and current

According to the rule of Faraday, the electrolytic substance amount is proportional to the quantity of electricity:

$$It = nzF \quad (7)$$

The oxygen generating volume can be calculated as following:

$$n = PV/RT \quad (8)$$

$$V = \frac{ItRt}{zFP} \quad (9)$$

V—gas volume, L; t—electrolysis time, s; R—gas constant, 0.08206 atm·L·mol^{-1}·K^{-1} T—gas temperature, K; Z—electron number of electrode reaction; F—Faraday constant, 9.648×10^4 C·mol^{-1}; P—atmospheric pressure, atm.

The measured volume is conversed to the state at 1

atm, 298 K and the partial pressure of water vapor must be emendated according to formula (10).

$$V' = \frac{P_t - P_{T,H_2O}}{P_0} \cdot \frac{298.15}{T} \cdot V \qquad (10)$$

V'—conversed gas volume, L; P_{T,H_2O}— partial pressure of saturation water vapor at the test temperature, atm. P_t——measured atmospheric pressure, atm. P_0—standard atmospheric pressure, atm.

According to equation (9), the oxygen amount, V_{4e}, through 4 electrons reaction process, is 3.80 ml·A^{-1}·min^{-1}. Correspondingly, V_{2e} is 7.61 ml·A^{-1}·min^{-1}. Measured value, V_t, can be expressed as:

$$V_t = V'/It \qquad (11)$$

Assume the percentage of 4 electrons reaction is X, and that of 2 electrons reaction is $1-X$, then the generated gas volume V_t is as following:

$$V_t = 7.61(1-x) + 3.80x \qquad (12)$$

$$x = (7.61 - V_t)/3.80 \qquad (13)$$

Thus the percentage of 4 electrons reaction can be calculated.

2.3 The influence of catalyst amount on the oxygen reduction

Four types of air electrode are made in which the catalyst MnO_2 content, showing in Tab. 1, is different.

Tab. 1　The catalyst content in the electrode

sample	A	B	C	D
Content of MnO_2/(%)	0	20	33	50

The state and variation of oxygen reduction process at the cathode were investigated. The results are shown in Fig. 2 and Fig. 3.

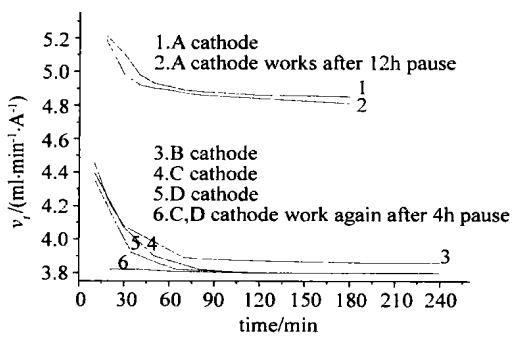

Fig 2　The variation of oxygen-generating amount with the electrolysis time

Fig. 2 shows that oxygen generating amount decreases with the electrolysis time when all the cathode sample work first time. The reason may be that the three-phase boundary of the porous electrode changes with the reaction time. The thickness of liquid film increases, leading to the higher diffusion resistance of reaction product, HO_2^- and OH^{-1}, diffusing to fluid phase. The other reason may be that the temperature of electrolytic system increases with working time and accelerates the reaction speed of chemical decomposing (Eq (3)). It manifests that the reaction trends Eq (4), for the reaction Eq (1) and Eq (2), Eq (1) and Eq (3) are equal to reaction Eq (4). The three-phase boundary of air cathode gradually turn to be stable when the air cathode work for 60 minutes, and the oxygen evolution at the cathode turns to be stationary.

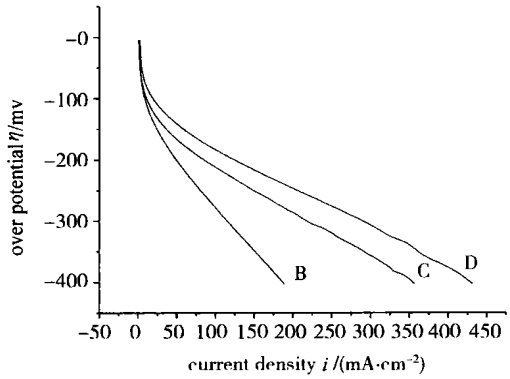

Fig 3　Polarization curve of the air electrode

The catalyst of air cathode A which forms peroxide is only active carbon. The percentage of 2e process reaction (Eq (1)) is 74% as shown in Fig. 2. The balance of reduction reaction on cathode A can be repeatedly got when the electrolysis set restarts after a certain time of pause, as line 2, but the time will be shorter and the oxygen evolution amount will decrease. It testified that the state of porous surface in the air cathode depends on the component of the air cathode and changes with the cathode reaction. The hydrophility of the porous surface in the air cathode enhances with the work time of the air cathode. This change will lead to the decrease of the synthesis efficiency of electrochemical reactor. So the technique can be used to evaluate the properties and life of the air cathode as a reference.

The three-phase interface in the porous structure will stable electrode can quickly become for hydrophilic catalyst is added in cathode B, C and D. There would be no apparent drop in the volume oxygen generated even at the very beginning of the process when the cathode works again, i.e. the three phase boundary would remain in a relatively stable state. It will get to a balance state at the beginning when the cathode works again. It means that the amount of product HO_2^- will not be much enough to influence the properties of the battery.

The percentage of reaction (4) in the air electrode can be increased through adding catalyst MnO_2 without regarding the intermediate process. Four electrons path reaction can't take place completely when the catalyst is

shortage (as air cathode B). The reaction of 4 electrons path is 97%. The polarization is great, for HO_2^-, the electrode reaction product, isn't decomposed completely. It is not fit for the usage in cell because a little of HO_2^- still exists in the electrolyte which will cause the anode passivation. All the reaction will follow the 4e path when the catalyst amount increases (as air cathode C and D) to a certain value and the polarization decreases (as line C, line D in Fig. 3). The difference of polarization voltage between the air cathode C and D is no more than 50 mV when the current density is lower than 100mA·cm^{-2}. But the content of catalyst in cathode D is much more than that in cathode C. The concentration of HO_2^- can decrease to minimum to prevent the anode from passivation for cathode C. Regarding the operation life of air electrode and manufacturing cost, cathode with lower catalyst content is manufactured. The open-circuit voltage and other properties of battery are not affected, for the working current density of zinc-air battery is usually below 100 mA/cm^2.

3 Conclusions

(1) Experiments show that the amount of oxygen evolution in the electrolysis indicates directly the degree of oxygen reduction. The percentage of the 2e or 4e path reduction reaction can be calculated through measuring the volume of the gas generated from an electrolysis bath and the current of the electrolysis bath with a given period of time

(2) The amount of carbon carrier and catalyst has much influence on the product of the oxygen reduction reaction at the cathode. The 2e path reduction reaction on the cathode covers 74 % with only active carbon as catalyst at 45 ~ 50 ℃ as working temperature when the reaction is stabilized. The reaction at air cathode will follow the 4e path when the concentration of catalyst MnO_2 is over 33%. The method can simulate the working state of the battery and electrochemical reactor and measure the final state of oxygen reduction in air electrode (without regard for the intermediate product and process) and the change of the electrode reaction with time.

References:

[1] TANG Y G, LU L B. The research of aluminum/air battery [J]. Acta Scientiarum Naturalium Universitatis Sunyatseni, 2003, 42 (6): 66—69

[2] HOSOYA T, KANAI T. Air electrode manufacturing method of air cell and air electrode [P], JP2001—313039.

[3] YANG C C. Preparation and characterization of electrochemical properties of air cathode electrode [J]. Internation Journal of Hydrogen energy, 2004, 29 (2): 135—143.

[4] BRILLAS E, MEAESRO A, MORATALLA M. Electrochemical extraction of oxygen from air via hydroperoxide ion [J]. J Appl Electrochem, 1997, 27 (1): 83—92.

[5] YANG M, SUN K P, DU J Q, et al. Synthesis of hydrogen peroxide through alkaline fuel cell reaction [J]. Journal of Beijing University of Chemical Technology, 2002, 29 (2): 91—93.

[6] FANG L G, LI J J, WANG H L. Study on the Electrochemical Extraction of Oxygen from Air [J]. Journal of South China University of Technology (Natural Science Edition), 2003, 31 (3): 85—88.

[7] PAN Z C, PEN Y Y. Electrosynthesis of sodium perborate using air cathode [J]. Journal of Chemical Industry and Engineering (China), 1996, 47 (6): 712—717.

[8] ALCAIDE F, BRILLAS E, CABOT P L. EIS analysis of hydroperoxide ion generation in an uncatalyzed oxygen-diffusion cathode [J]. Journal of Electroanalytical Chemstry, 2003, 547 (4): 61—73.

[9] MORIMTO T, SUZUKI K, MATSUBARA T, et al. Oxygen reduction electrode in brine electrolysis [J]. Electrochimica Acta, 2000, 45: 4257—4262.

[10] LU Z E. The theory and application of electrode process [M], Publishing Company of Higher Education, 1992, 137—138.

空气电极氧还原过程研究

欧秀芹, 梁广川, 解 飞, 范 飞, 刘曙光

(河北工业大学能源与环境材料研究所, 天津 300131)

摘 要: 通过测量空气阴极与镍阳极组成的电解析氧装置的氧气产出量, 并根据单位时间内气量与电流的关系可定量地计算出氧还原的两种历程在反应中所占的比例。试验结果表明, 仅以活性炭为电催化剂的空气电极 2 电子途径的反应占 74%, 以 MnO_2 为催化剂的空气电极, 当含量达 33%时, 4 电子途径的反应达 100%。此方法可动态研究反应过程中两种氧还原反应随时间的变化。

关键词: 氧还原; 反应历程; 空气电极; 催化剂

中图分类号: O646.21