ELSEVIER

Journal of Power Sources 91 (2000) 83–85

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

Carbon-based air electrodes carrying MnO_2 in zinc–air batteries

Zidong Wei *, Wenzhang Huang, Shengtao Zhang, Jun Tan

Department of Applied Chemistry, Chongqing University, Chongqing 400044, People's Republic of China

Received 19 April 1999; received in revised form 14 September 1999; accepted 14 January 2000

Abstract

Catalysts prepared from the carbon black impregnated with manganous nitrate solution and then heated at temperature from 270°C to 450°C were investigated. It was found that the impregnated catalysts heated at temperature of 340°C exhibited the best catalytic activity for oxygen reduction in alkaline electrolyte. It was also found that the XRD spectra of pyrolytic MnO_2 from manganous nitrate over 340°C were different from those below 340°C. The enhanced catalysis of air electrodes was ascribed to the formation of MnO_2 crystal with *d*-value of 2.72 Å as the impregnated-catalysts was heated at temperature of 340°C. The other factors in preparation of air electrodes were also discussed.

Keywords: Air electrodes; Manganese dioxide; Zinc–air batteries

1. Introduction

Among metal–air batteries, the zinc–air battery has attracted a particular attention. The zinc–air battery has been developed as a practical, high-energy density power supply. Air cathode research and development all over the world has resulted in substantial improvement of zinc–air systems. A major breakthrough in air cathodes was the development of various alternatives as a replacement for platinum, e.g. manganese dioxide, cobalt tetramethoxy porphorin, perovskite-type oxides [1–3] etc. However, its power density is still limited primarily by the high polarization of air cathodes that are ascribed to a slow electrocatalytical reduction of oxygen. Among the alternatives for platinum catalysts, MnO_2 shows some promise of success due to its low cost and its high catalytic activity for the oxygen reduction. However, the recommended technical parameters associated with the fabrication of MnO_2 catalyzed air electrodes varies from one report to another. For instance, one source [1] suggested the pyrolytic temperature of manganous nitrate to be 500°C, while another [4] recommended 270°C. The pore-forming filler for air electrodes was adopted in reference [1], but the authors' previous work [5] showed that it is not necessary when the current density is around 50 mA/cm^2.

In this paper, a new phenomenon is reported during searching the optimum pyrolytic temperature of manganous-nitrate-impregnated carbon blacks. An enhanced catalysis of an air electrode was observed on the electrode containing a favorable MnO_2 crystal with *d*-value of 2.72 Å. The other parameters critical to obtaining a good air electrode are also discussed.

2. Experimental

Carbon-based electrodes were prepared using techniques described previously [6]. One of the two catalyst carriers was SL-30 carbon black with specific area of 270 m^2/g (Zigong carbon black, China), the other one was acetylene black (AB) with a specific area of 70 m^2/g. When a mixture of two carbon powders were used, the weight ratio of the two kinds of carbon powders was 1:1. Carbon powders were first wetted with alcohol and then mixed thoroughly with a reagent grade of 65 wt.% manganous nitrate solution at room temperature to form a slurry. The slurry was dried and then ground. The sample was then calcined at a certain temperature for an hour. Teflon-30 suspension was served as a wet-proofing agent and binder. The contents of solid Teflon-30 in a catalyst layer and a gas diffusion layer were 25 wt.% relative to the catalyzed carbon and 33 wt.% to AB. Only AB was utilized in the gas diffusion layer, which is also called a wet-proofing layer in this paper. The mixture of carbon

* Corresponding author. Tel.: +86-23-65106253.
E-mail address: zdwei@cqu.edu.cn (Z. Wei).

0378-7753/00/$ - see front matter
PII: S0378-7753(00)00417-1

powders catalyzed by MnO_2 or not, Teflon-30 suspension and alcohol were rolled to 0.3 mm. The alcohol and water in Teflon suspension also served to formation of the pores of air electrodes. A three-layered air electrode was prepared by pressing "catalyst layer/wet-proofing layer/nickel-plated copper screen/wet-proofing layer" togetherat a pressure of 80 kg/cm^2 and then was sintered at a temperature of 280°C. The final air electrode is 0.8 mm in thickness. A two-layered air electrode was prepared by the same procedure as the three-layered electrode unless the wet-proofing layer next to the catalyst layer was omitted.

The quasi steady-state discharge curves of zinc–air batteries were measured in double-electrode system by linear sweeping current in 7 mol/l KOH in atmosphere. The anode is the pure zinc (99.95%). The measurements were performed at room temperature (about 17°C).

As MnO_2-catalyzed carbon powders were served as the samples of XRD investigation, many peaks assigned to carbon powders will completely cover the peaks to MnO_2. In order to avoid the interference of carbon on XRD spectra of pyrolytic MnO_2, samples, which do not contain carbon, were prepared following the similar procedure to the manganous-nitrate-impregnated carbon blacks. All the XRD spectra in this paper refer to the pyrolytic products of manganous nitrate.

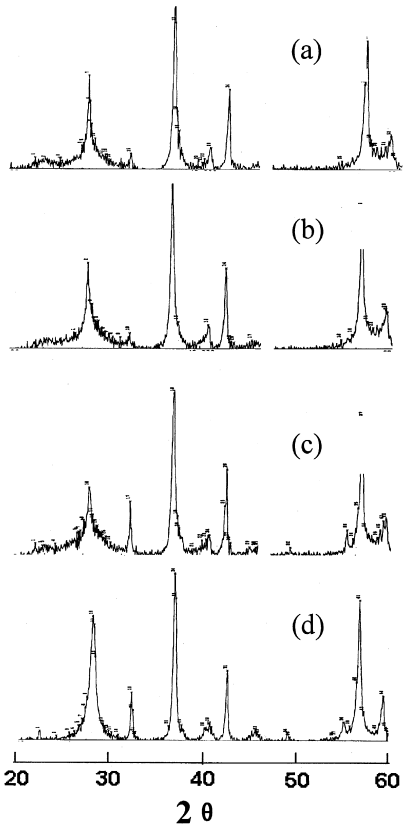

Fig. 2. XRD spectra of MnO_2 from the pyrolysis of manganous nitrate at (a) 270°C, (b) 300°C, (c) 340°C and (d) 450°C.

3. Results and discussion

The effect of heat treatment of carbon black impregnated with manganous nitrate on the electrochemical performance of air electrodes is shown in Fig. 1 together with the electrode made from direct mixture of electrolytic MnO_2 powders and with the electrode made from only carbon as comparisons. It is found that the pyrolytic MnO_2 from manganous nitrate-impregnated carbon blacks at the temperature of 340°C exhibited the best performance. The electrodes illustrated in Fig. 1 were fabricated under the same conditions except pyrolyzing temperature for MnO_2 formation. As known, the influences of temperature on crystalline formation are diverse. In addition to determining which kind of materials is produced at a certain temperature, it also determines which type of crystalline of the same material will be. The XRD spectra of the samples heated at different temperatures are illustrated in Fig. 2. A markedly increased peak in XRD spectrum of pyrolytic MnO_2 over 340°C was observed at 33.3° of 2θ. This peak is representative of the MnO_2 crystal with d-value of 2.72 Å. It seems reasonable to attribute the outstanding catalytic activity of the electrode to the formation of the crystalline

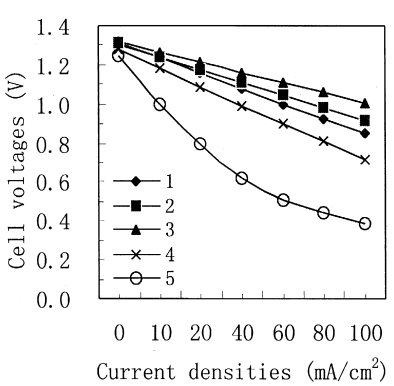

Fig. 1. Cell voltages vs. current densities for zinc–air batteries in 7 mol/l KOH with porous carbon-based air cathodes containing 6.7 wt.% MnO_2 prepared from manganous nitrate-impregnated-carbon black heated at (1) 300°C, (2) 280°C, (3) 340°C, (4) from direct mixture of electrolytic MnO_2 and (5) containing no MnO_2 as comparison.

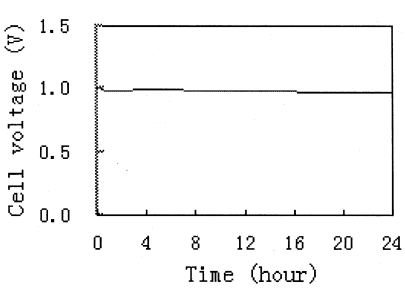

Fig. 3. Discharge behaviour of zinc–air battery at 40 mA/cm^2 for an optimized air electrode.

Table 1
Influence of the preparation parameters of air electrodes on the cell voltage (V) of zinc–air batteries at the given current densities

I (mA/cm^2)	Loading of MnO_2 on air electrode (wt.%)[a]			Layers of air electrodes		Composition of carbon black[b]		
	10	6.7	5	3	2	SL-30	AB	Mixture
20	1.13	1.24	1.19	1.22	1.19	1.28	1.24	1.24
50	0.98	1.12	1.05	1.06	1.02	1.18	1.12	1.14
100	0.72	0.95	0.82	0.83	0.74	1.04	0.96	0.98

[a] MnO_2 was prepared from the pyrolysis of manganous of nitrates adsorpted on a mixture of AB and SL-30 carbon blacks.
[b] The loading of MnO_2 is 6.7 wt.% for all cases.

grain of MnO_2 with d-value of 2.72 Å, which surely plays a critical role in catalysis of oxygen reduction. The catalyst MnO_2 obtained at 450°C also has the same XRD spectrum as that at 340°C, but its catalytic activity is not as good as that at 340°C.

The following two cases probably prevent electrolytic MnO_2 powders from showing a good catalytic activity for oxygen reduction; first, the poor distribution of MnO_2 on carbon black resulting from the direct mixture of the two solid powders, second, the crystalline type of electrolytic MnO_2 not fitting to catalysis of oxygen reduction. The spectra of electrolytic MnO_2 collected by Kozawa [7] did not show the abovementioned crystalline.

The influence of the other preparation parameters on the performance of air electrodes is summarized in Table 1. It is worth noting that the electrode with a structure of "three-layer" showed a better performance than that with a structure of "two-layer". It means that the wet-proofing layer not only decreases resistance to gas diffusion, but also improves the gas distribution at the interface of the catalyst layer and wet-proofing layer. The higher specific surface area of carbon black is helpful to obtain a better dispersion of catalyst on it and in turn improve the performance of air electrode made from it. However, the air electrodes made from carbon black with a higher specific surface area was more easily broken during handling than that with a lower specific surface area. The mechanical strength of electrode made from the mixture of the two abovementioned carbon blacks was acceptable. Of all factors, the most critical is the loading of MnO_2 on carbon powder. It can be seen from Table 1 that there is an optimum amount for MnO_2 loading on carbon black in view of polarization.

Fig. 3 shows the long-term performance of an air electrode fabricated at the optimized conditions at 40 mA/cm^2. It can be seen that the performance of the electrode is quite stable.

4. Conclusion

The improved performance of an air electrode catalyzed by MnO_2 has been achieved as the following conditions are followed.

(1) The pyrolyzing temperature of carbon black impregnated with manganous nitrate is kept at 340°C for an hour. At this temperature, a favorable MnO_2 crystal with d-value of 2.72 Å is generated, which is highly catalytic to oxygen reduction.

(2) The optimum loading of MnO_2 on carbon black is about 6.7 wt.% based on the weight of carbon black.

(3) The structure of air electrode with "three-layer" is preferable to that with "two-layer".

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC) under grant no. 2997604.

References

[1] J. Lamminen, J. Kivisaari, M.J. Lampinen, M. Viitanen, J. Vuorisalo, J. Electrochem. Soc. 138 (1991) 905.
[2] M. Yoshino, S. Noya, A. Hanabusa, N. Yanagihara, Jp 04 02 046, 1992.
[3] A. Hanabusa, S. Noya, M. Yoshino, N. Yanagihara, Jp 04 17 259, 1992.
[4] Zhihui Liu, Zhenya Li, Chin. J. Power Sources 17 (1993) 7.
[5] Zidong Wei, Hetong Guo, Zhiyuan Tang, Acta Phys. Chim. Sinica 12 (1996) 1022.
[6] D.B. Zhou, H.V. Poorten, Electrochim. Acta 40 (1995) 1819.
[7] A. Kozawa, Handbook of MnO_2, Sichuan Press of Science and Technology, 1993, pp. 87–99.