Journal of Applied Electrochemistry **30**: 1133–1136, 2000.

Induced effect of Mn_3O_4 on formation of MnO_2 crystals favourable to catalysis of oxygen reduction

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Received 7 February 2000; accepted in revised form 22 May 2000

Key words: air electrodes, MnO_2 catalyst, Mn_3O_4 catalyst, zinc–air battery

Abstract

Catalysts prepared from a mixture of Mn_3O_4 powders and carbon blacks carrying pyrolytic MnO_2 were investigated for catalysis of oxygen reduction. It was found that the introduction of Mn_3O_4 to the pyrolysis process of manganous nitrate carried out on carbon blacks improved the performance of air electrodes as the amount of Mn_3O_4 was controlled within 15 wt % relative to the weight of carbon carrier. The mechanism of this improved behaviour was also investigated using X-ray diffraction (XRD). The results showed that Mn_3O_4 induced the formation of favourable MnO_2 crystalline grains during the pyrolysis of manganous nitrate. The induced effect and the blocking effect of Mn_3O_4 on the catalysis of air electrodes catalysed by pyrolytic MnO_2 were demonstrated both on carbon black and porous carbon carriers.

1. Introduction

MnO_2 catalysed air electrodes have been used as cathodes in metal–air batteries with some success [1]. However, the activation polarization for electrocatalysts including platinum [2], the best catalyst to date, has been the primary problem preventing the wide use of chemical energy conversion devices associated with air electrodes. The current catalysts for oxygen electroreduction leave much to be desired regarding the reversible potential of oxygen reduction. Mn_3O_4 alone, or as a mixture with Mn_5O_6, has also been reported as a catalyst for carbon-based air electrodes [3, 4]. Their electroactivities were claimed to be good, but the authors' experiments demonstrated that the electrochemical activity of such electrodes catalysed by Mn_3O_4 was no better than that of carbon-based air electrodes with no additional catalysts (see Fig. 1). Unexpectedly, the 'special' mixture of MnO_2 and Mn_3O_4 had a very high activity for oxygen reduction. Moreover, this enhanced effect only appeared when Mn_3O_4 participated in the pyrolysis. X-ray diffraction studies showed that the presence of Mn_3O_4 induced the formation of a special crystalline MnO_2 grain during the pyrolysis of manganous nitrate. This special crystalline grain had the same XRD pattern as reported earlier [5], but the critical XRD peak of MnO_2 increased much more in the presence of Mn_3O_4 than MnO_2 alone when formed at elevated temperature.

2. Experimental details

A 50:50 (w/w) mixture of carbon black SL-30 (Zigong Carbon Black Co., China) having a specific surface area of 270 $m^2\ g^{-1}$, and acetylene black (AB) having a specific surface area of 70 $m^2\ g^{-1}$ were used as the catalyst carriers. Another catalyst carrier, Porous Carbon (PC), having a specific surface area of 500 $m^2\ g^{-1}$ was also used to investigate the mechanism of the enhancement effect of Mn_3O_4. Unlike SL-30 and AB, much of the specific surface area of PC is attributable to the wall surfaces of inner pores in the PC powder rather than the outside surface of the powder. The catalyst carrier (a mixture of SL-30 and AB or PC) was first wetted with alcohol, and then mixed thoroughly with reagent grade manganous nitrate solution and the required amount of Mn_3O_4 powder (industrial grade) with a diameter less than 2 μm. The slurry was dried and ground, then calcined at 340 °C for 1 h. The final catalyzed carbon powder contained 6.7 wt % MnO_2 relative to the carbon carrier and different loadings of Mn_3O_4.

A catalyst containing MnO_2 or Mn_3O_4 alone was prepared by the same procedure as mentioned above when either Mn_3O_4 or 65% manganous nitrate was used in the preparation. The pyrolysis process was unnecessary if manganous nitrate was omitted.

A Teflon-30 suspension was used as a wet-proofing agent and binder. The solid content of Teflon-30 in the catalyst layer and the gas diffusion layer was 25 wt % relative to the catalysed carbon powders and 33 wt % relative to AB, respectively. Only AB was utilized in the diffusion layer. A dough consisting of a mixture of catalysed carbon powder, Teflon-30 suspension and alcohol was rolled to 0.3 mm. At the same time, the alcohol and water in the Teflon suspension also served as the pore generator of the air electrodes. A three-layer air electrode was prepared by pressing 'catalyst layer/wet-proofing layer/nickel-plated copper screen (current collector)/wet-proofing layer' together at a pressure of 80 kg cm^{-2}, then sintering at 280 °C. The final air electrode was 0.8 mm in thickness.

The quasi-steady state discharge curves of zinc–air batteries were measured in a double-electrode system by linear current sweeping in 7 M KOH in air. The anode was a pure zinc sheet (99.95%). The measurements were performed at room temperature (about 12 °C). Long run tests were conducted with regular renewal of the zinc anode and electrolyte.

The manganese oxide–catalysed carbon powders were investigated by XRD, generating scans wherein the peak intensities generated from the carbon powders completely overshadowed the manganese oxide peaks. To subtract such interference from the carbon signals, the samples of manganous nitrate alone or with Mn_3O_4 were heated according to the same procedure as the impregnated carbon blacks. All XRD traces in this paper refer to the manganese oxides.

3. Results and discussion

The short-term polarization curves of carbon-based air electrodes with mixtures of Mn_3O_4 and pyrolytic MnO_2 are shown in Figure 1, together with curves for air electrodes catalyzed by only MnO_2 or Mn_3O_4 as comparisons. The electrochemical activity of air electrodes catalysed by manganese oxides increases with addition of Mn_3O_4 up to about 15 wt % Mn_3O_4, and then decreases with further addition. Previously [5], we reported that the pyrolysis of manganous nitrate at 340 °C led to the formation of a special crystalline MnO_2 grain which is beneficial to the catalysis of oxygen reduction. The same formation of special MnO_2 was also observed in the presence of Mn_3O_4 in manganous nitrate pyrolysis, as shown in Figure 2. The influence of pyrolysis temperature and Mn_3O_4 on the typical peaks in the MnO_2 XRD pattern is shown in Table 1. In addition to strengthening the XRD peaks of MnO_2 at 32.86° and 55.12° (2θ, d-values 2.72 Å and 1.66 Å, respectively), the presence of Mn_3O_4 during manganous nitrate pyrolysis also reduced the MnO_2 XRD peak intensities at 37.28° and 56.76° (2θ, d-values 2.41 Å and 1.62 Å, respectively).

The induced effect of Mn_3O_4 on the formation of favourable MnO_2 crystals was also confirmed in an experiment in which porous carbon (PC) replaced the

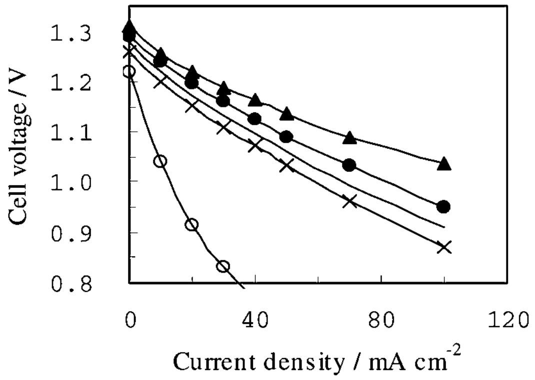

Fig. 1. Influence of Mn_3O_4 on 6.7 wt % MnO_2-catalysed carbon black electrodes for oxygen reduction in 7 mol L^{-1} KOH at 12 °C with the loading of Mn_3O_4 based on carbon black (—) 0, (●) 8 wt %, (▲) 15 wt %, (×) 20 wt %, (○) 15 wt % but no MnO_2 catalysts.

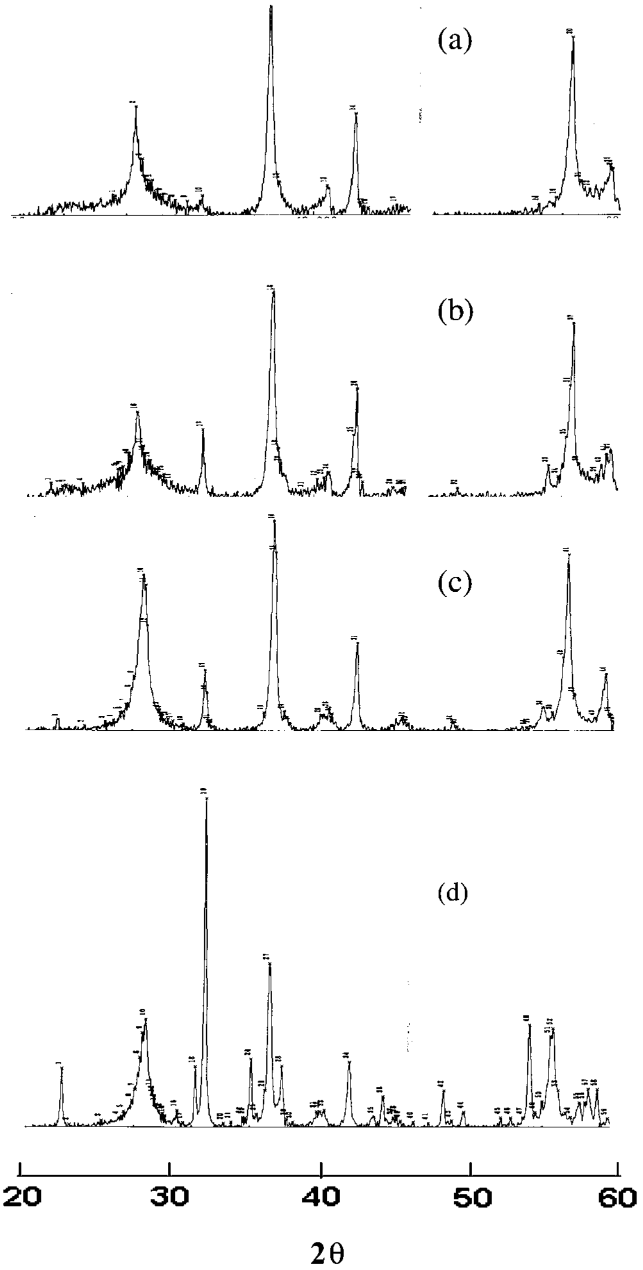

Fig. 2. XRD spectra of MnO_2 from the pyrolysis of manganous nitrate at (a) 300 °C, (b) 340 °C, (c) 450 °C, (d) 340 °C but in the presence of Mn_3O_4.

Table 1. Influence of temperature and Mn_3O_4 on XRD spectra of MnO_2 made from pyrolysis of manganous nitrate

2θ	*d*-value/Å	I/I_0 at different pyrolysis temperatures				
		270 °C	300 °C	340 °C	450 °C	340 °C plus Mn_3O_4
23.08°	3.84	7	5	7	6	18
32.86°	2.72	10	9	34	29	100
37.28°	2.41	100	100	100	100	50
55.12°	1.66	9	8	16	12	32
56.78°	1.62	75	76	86	85	30
28.64°	3.11	55	47	42	75	33
42.78°	2.11	47	44	54	42	20

carbon black, that is, SL-30 and AB, as the catalyst carrier. The results are shown in Figure 3, which shows that the addition of Mn_3O_4 does not improve the MnO_2-catalysed porous carbon electrodes for catalysis of oxygen reduction. One of the main differences between the carbon black (SL-30 and AB) and PC carriers lies in the contribution of the specific surface area almost completely from the outside surface of the carbon black for SL-30 and AB, but mostly from the inner pore wall on porous carbon for PC. When PC was impregnated with manganous nitrate solution, most of the manganous nitrate was adsorbed on the wall of the inside pores of PC, but the absorption of Mn_3O_4 powders only took place on the outside surface of PC because the small mouths of the inner pores of PC blocked the Mn_3O_4 powder entering the inside pores. Therefore, the high mingling between manganous nitrate and Mn_3O_4 powders did not occur on porous carbons as it did on carbon blacks. The Mn_3O_4 attached to the outside surface of PC did not participate in the pyrolysis of $MnNO_3$ adsorbed on the inside wall of the inner pores. Naturally, the induced effect of Mn_3O_4 on the formation of MnO_2 crystal to catalyse oxygen reduction did not take place on porous carbons as it did on carbon blacks. Conversely, the excessive amount of Mn_3O_4 would blocked the mouth of the inner pores of PC, thus interrupting the contact between electrolyte and the MnO_2 catalyst on the inside wall of the inner pores. This blocking effect causes a decline in the electrochemical activity of manganese oxide-catalyzed air electrodes, as shown in Figure 3. The decline in electrochemical activity can also be observed on the electrode made from the manganese oxide-catalysed carbon black, once the loading of Mn_3O_4 surpasses a critical value, as shown in Figure 1. Under this circumstance, the blocking effect of Mn_3O_4 will exceed its induced effect on forming a favourable MnO_2 crystal for catalysis of oxygen reduction.

Based on the above analysis, a further two experiments were carried out on carbon black carriers. The results are shown in Figure 4. Apparently, no enhanced effect was observed when the Mn_3O_4 was directly added to the 6.7 wt % MnO_2-catalysed carbon blacks. The behavior of curve (○) in Figure 4 is almost the same as that of curve (–) in Figure 1, which represents the performance of the electrode catalysed by MnO_2 alone. This means that the 'induced effect' of Mn_3O_4 only happens during the formation of MnO_2 by means of the pyrolysis of manganous nitrate. This induced effect led to the formation of MnO_2 with *d*-values of 2.72 Å and 1.66 Å. This type of MnO_2 is favourable for the catalysis of oxygen reduction. Such an induced effect of Mn_3O_4 may be due to the fact that Mn_3O_4 and MnO_2 have the same crystal type, γ-type. In the XRD pattern of Mn_3O_4, the second strongest diffraction peak is the peak with *d*-value 2.77 Å [6], which is nearly equal to 2.72 Å, one of the *d*-values of the MnO_2 favourable for oxygen reduction.

Figure 5 shows the long-term performance of an air electrode catalysed by Mn_3O_4-induced MnO_2 at 40 mA cm^{-2}. It can be seen that the performance of the electrode is quite stable. The dramatic jumps of the curve are due to the adoption of an enlarged potential scale.

4. Conclusion

There are two favourable MnO_2 crystalline forms for oxygen reduction. Their corresponding *d*-values are

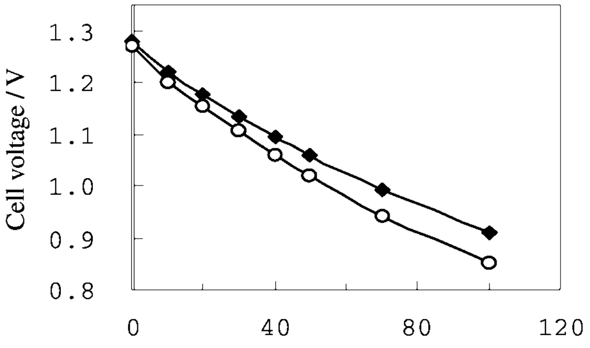

Fig. 3. Influence of Mn_3O_4 on 6.7 wt % MnO_2-catalysed porous carbon electrodes for oxygen reduction in 7 mol L^{-1} KOH at 12 °C with the loading of Mn_3O_4 based on porous carbon (◆) 0 ~ 10 wt %, (○) 15 wt %.

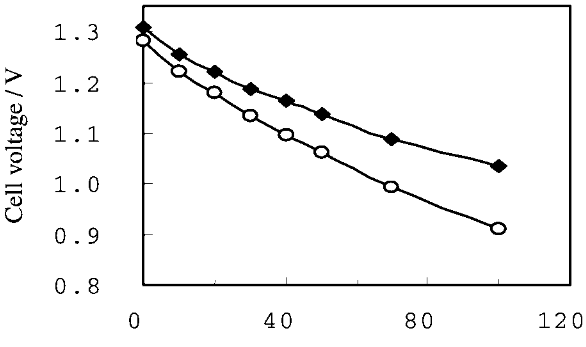

Fig. 4. Influence of 15 wt % Mn_3O_4 on 6.7 wt % MnO_2-catalysed carbon black electrodes for oxygen reduction in 7 mol L^{-1} KOH at 12 °C. Mn_3O_4 added before (◆) and after (○) the pyrolysis of manganous nitrate-impregnated carbon blacks at 340 °C.

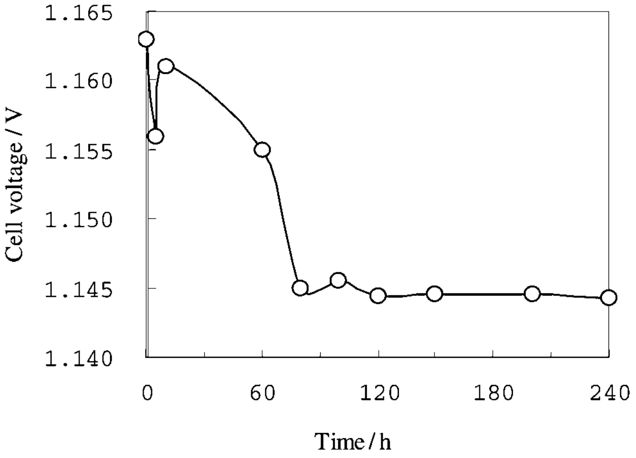

Fig. 5. Discharge behaviour of the zinc–air battery with Mn_3O_4-induced MnO_2–air electrode at 40 mA cm^{-2}.

2.72 Å and 1.66 Å, respectively. The electrochemical activity of air electrodes catalysed by Mn_3O_4 alone is no better than that of carbon-based air electrodes without other catalysts. However, Mn_3O_4 can induce the forming of the favourable MnO_2 crystals during the pyrolysis of manganous nitrate. There is a threshold for the addition of Mn_3O_4 in manganous nitrate–impregnated-carbon black. The electrochemical activity of the electrode made from the manganese oxide–catalysed carbon black will decline once the loading of Mn_3O_4 surpasses this threshold because the blocking effect of Mn_3O_4 is dominant. The induced effect of Mn_3O_4 does not take place if porous carbon is employed as the catalyst carrier instead of the carbon black. It is necessary that Mn_3O_4 participates in the pyrolysis process of manganous nitrate.

Acknowledgement

Financial support from the National Natural Science Foundation of China (NSFC) under Grant No. 2997604 is gratefully acknowledged.

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