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Transition metal oxides based oxygen electrodes in alkaline solution-Physicochemical and electrochemical characterisation

I Arul Raj, V V Giridhar and K I Vasu
Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

Electrolytic manganese dioxide (EMD, CECRI) dispersed with lanthanum/praseodymium/dysprosium through thermal route in selected nonstoichiometric compositions have been prepared and their physicochemical characteristics are reported. The electrochemical activities of these oxide materials for the oxygen evolution and oxygen reduction processes in alkaline solution are presented.

Key words: Oxide materials, alkaline solution, oxygen evolution and reduction reactions

INTRODUCTION

This investigation has been undertaken to examine the electrochemical activity of EMD towards oxygen electrode reactions in alkaline medium, when dispersed with rare earth metals such as lanthanum, praseodymium/dysprosium in selected nonstoichiometric compositions, through thermal route, as no systematic attempt has been made so far in this direction.

EXPERIMENTAL

Electrode materials

The electrochemical method to prepare the EMD had been dealt with in [1]. The rare earths were dispersed onto EMD by heating the mixtures of oxides at 1270 K for 48 hours.

Test electrodes fabrication

Respective oxide powders were mixed with PTFE (Du Pont) suspension in isopropanal medium in the weight ratio of six to one, powder to binder. The resulting paste was painted onto smooth Glassy Carbon (GC) discs, to obtain a thin adherent coating.

Electrochemical measurements

The cyclic voltammograms were obtained using PAR Model 370 Electrochemistry System. The steady state experiments were carried out potentiostatically. Large are Pt foil and Hg/HgO, OH^- were used as counter and reference electrodes respectively.

RESULTS AND DISCUSSION

The physicochemical characteristics of the oxide materials are presented in Table I. The average particle size ranges from 7 to 14 μm. The specific surface area of the oxide powders is significantly small when compared with that of similar oxides obtained through freeze-drying methods [2].

TABLE–I: Physicochemical characteristics of lanthanum manganates

Oxide sample	Average particle size (μm)	Specific surface area ($m^2.cm^{-3}$)	Bulk density ($gm.cm^{-3}$)
$La_{0.1}MnO_3$	13.4	0.11	1.2667
$La_{0.2}MnO_3$	13.6	0.10	1.4490
$La_{0.5}MnO_3$	9.6	0.12	1.7113
$LaMnO_3$	9.3	0.13	1.8643

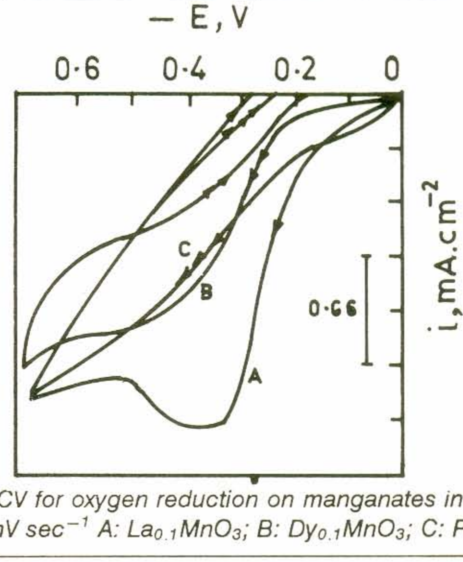

Fig. 1: LSCV for oxygen reduction on manganates in 1M KOH, 301K 10 mV sec^{-1} A: $La_{0.1}MnO_3$; B: $Dy_{0.1}MnO_3$; C: $Pr_{0.1}MnO_3$

Figure 1 shows the cyclic voltammograms corresponding to oxygen reduction on the rare earths based manganates. Figure 2 shows the cyclic voltammograms corresponding to oxygen reduction on lanthanum manganates. The behaviour of lanthanum-dispersed manganates are markedly different among themselves as a function of lanthanum content. This apparent variation observed in the

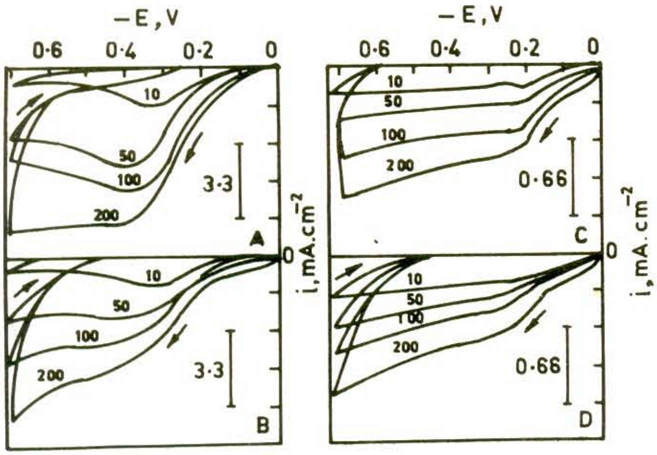

Fig. 2: LSCV for oxygen reduction in 1M KOH, 301K - Different sweep rates. A: $La_{0.1}MnO_3$; B: $La_{0.2}MnO_3$; C: $La_{0.5}MnO_3$; D: $LaMnO_3$

voltammetric characteristics among these manganates is attributed to the different quantum of structural distortion brought about by the insertion of lanthanum in EMD lattice in different nonstoichiometric compositions. The validity of this argument has already been established in the case of lanthanum-alkaline earth based manganates [3].

CONCLUSION

The electrochemical stability of lanthanum manganates is good. The use of an appropriate binding material in order to fabricate porous electrodes from these oxides needs to be investigated to ascertain their application as electrocatalysts in alkaline fuel cell/water electrolyzers.

REFERENCES

1. V Aravamudhan, S Visvanathan, J P R Raj, S Kulandaisamy and S Chockalingam, *Proc 2nd Int Symp Industrial and Oriented Basic Electrochemistry, SAEST, INDIA*, Dec (1980) 2.5 and 2.6

2. J O' M Bockris, T Otagawa and V Young, *J Electroanal Chem*, **150** (1983) 633

3. I Arul Raj, K V Rao and V K Venkatesan, *Bull Electrochem*, **2** (1986) 157