Bull. Mater. Sci., Vol. 6, No. 2, May 1984, pp. 259–261. © Printed in India.

MnO_2 catalyzed carbon electrodes for dioxygen reduction in concentrated alkali

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Abstract. A process to deposit γ-MnO_2 catalytic oxide onto coconut-shell charcoal substrate is described. Current-potential curves for electroreduction of dioxygen with electrodes fabricated from this catalyzed substrate are obtained in 6M KOH under ambient conditions. The performance of these electrodes is competitive with platinized carbon electrodes.

1. Introduction

Efficient reduction of oxygen under ambient conditions is a reaction of great importance for fuel-air fuel cells and metal-air batteries (Bockris *et al* 1981). The development of a low cost electrocatalyst capable of reducing oxygen reversibly is a challenge of the present day oxygen electrochemistry.

In recent years, several metal oxides have been explored as electrocatalysts for dioxygen reduction in alkaline media (Egdell *et al* 1983; Horowitz *et al* 1983; Trasatti 1980). Manganese dioxide which is readily available and is cheap enough (Sathyanarayana and Sridharan 1976) has been claimed to be a promising oxide catalyst for the electroreduction of oxygen (Armstrong 1975). This oxide catalyst exists in several forms. Of these, the oxygen-deficient γ-MnO_2 possesses the maximum catalytic activity (Brenet 1979; Trasatti 1980). Electrocatalytic activity of γ-MnO_2 towards oxygen reduction has been explained by Brenet (1979) in light of the redox couples (Mn^{4+}/Mn^{3+}) through the following mechanism:

$$Mn^{4+} \xrightarrow{\bar{e}} Mn^{3+} \xrightarrow{O_2(ads)} Mn^{4+} + O_2^-(ads).$$

This material, however, has certain drawbacks such as its low surface area and the poor electrical conductance. These problems could easily be overcome by depositing it onto a conducting and high surface area carbon substrate. This paper describes an attempt to deposit the appropriate amount of γ-MnO_2 catalyst onto the coconutshell charcoal substrate and the electrochemical performance of the electrodes fabricated from such a substrate for dioxygen reduction in concentrated alkali.

Contribution No. 252 from the Solid State and Structural Chemistry Unit.

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2. Experimental

2.1 *Deposition of γ-MnO_2 onto the carbon substrate*

The chemical method adopted to prepare γ-MnO_2 catalytic oxide is similar to that described by Gattow and Glemser (1961). $KMnO_4$ containing desired weight percent of MnO_2 was dissolved in distilled water and mixed with an appropriate quantity of the carbon substrate to form a thick slurry. Freshly prepared sulphurous acid obtained by saturating water with sulphur dioxide was added to this slurry with constant stirring. The resultant mass was filtered, washed repeatedly and dried in an air oven at about 80°C. The process resulted in the deposition of γ-MnO_2 onto the carbon substrate. Formation of γ-MnO_2 catalytic oxide was ascertained by x-ray powder diffraction. A diffused diffraction pattern characteristic of amorphous γ-MnO_2 was obtained (Zwicker *et al* 1962).

2.2 *Preparation of the electrodes*

Electrodes of various carbon specimens were prepared by hot pressing the γ-MnO_2 deposited carbon substrate at 140°C at an optimized pressure of 0·05 ton/cm^2 on expanded platinum metal screens with 20% polythylene as binder. The detailed procedure of fabricating such electrodes is described elsewhere (Manoharan and Shukla 1983).

2.3 *Measurements of the electrochemical performance of the electrodes*

The electrochemical cell designed to measure the polarization performance contained the porous carbon working electrode catalyzed with γ-MnO_2, Hg/HgO, OH^- reference electrode equipped with a luggin capillary, a high surface area flat bed counter electrode made from sintered nickel and a magnetic stirrer submerged in 6M KOH electrolyte. The details of the electrochemical assembly have been described earlier (Manoharan and Shukla 1983). The cell assembly had a gas compartment on the rearside of the working electrode which was sealed by making the current collecting metal block press tightly against the electrode.

Galvanostatic polarization studies were carried out using a regulated dc power supply and a high-power rated rheostat in series with the electrochemical cell.

3. Results and discussions

The room temperature (~ 30°C) polarization curves for carbon electrodes with various loading levels (2, 4 and 8 wt%) of γ-MnO_2 catalyst at a gas pressure of 130 mm Hg are shown in figure 1. For comparison the polarization curves for the bare (without any catalyst) and 7 wt% Pt catalysed carbon electrodes are also shown in the figure. These curves are experimentally obtained and are not IR corrected. The experiments were repeated with a minimum of two electrodes each time and were reproducible. The electrocatalytic activity of γ-MnO_2 deposited carbon electrodes increased with decrease in its loading concentration. A 2 wt% of the oxide catalyst deposited onto the carbon substrate showed the maximum activity. This signifies that only an appropriate amount of oxide catalyst is required to be deposited onto the carbon substrate in order to facilitate the catalytic action without increasing the mass transfer and ohmic

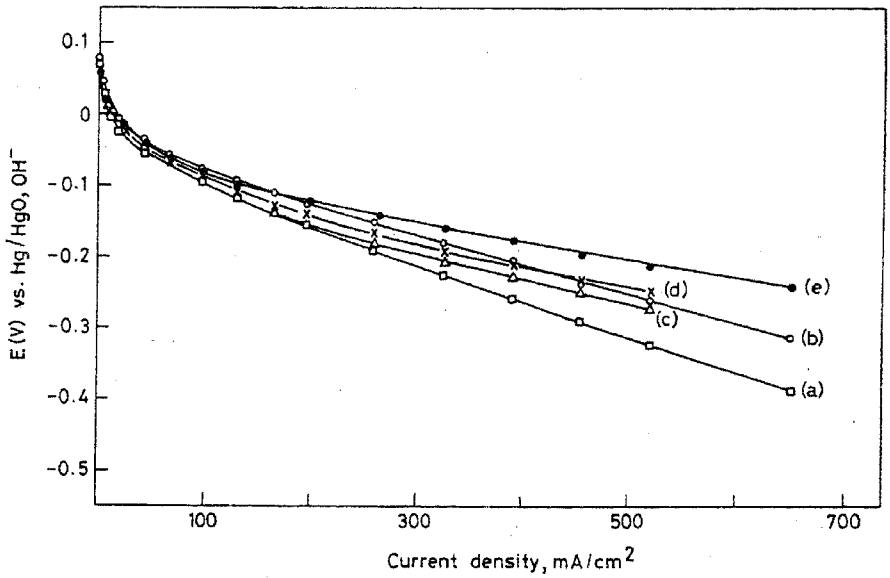

Figure 1. Current-potential curves for the electroreduction of dioxygen on (**a**) bare carbon electrode, (**b**) a 7 wt % Pt catalyzed carbon electrode, (**c**) a 8 wt % (**d**) a 4 wt % (**e**) a 2 wt % γ-MnO_2 catalyzed carbon electrode.

polarization components. The activity for dioxygen reduction on the carbon electrodes catalyzed with 2 wt % of γ-MnO_2 is competitive with the 7 wt % platinized carbon electrodes. The 2 wt % γ-MnO_2 catalyzed carbon electrode could be loaded with a current density of 650 mA/cm^2 at the polarization potential of $-0{\cdot}24$ V *vs* Hg/HgO, OH^-. To avoid the cathodic reduction of γ-MnO_2 catalyst (Sathyanarayana and Sridharan 1976) (which takes place at $-0{\cdot}3$ V *vs* Hg/HgO, OH^-) the electrodes were not subjected to polarization beyond this potential.

Acknowledgement

Authors are thankful to Prof C N R Rao for inviting them to contribute this article. Financial support from DST is gratefully acknowledged.

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