

MnO₂ catalyzed carbon electrodes for dioxygen reduction in concentrated alkali

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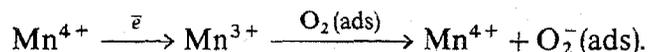
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Abstract. A process to deposit γ -MnO₂ catalytic oxide onto coconut-shell charcoal substrate is described. Current-potential curves for electroreduction of dioxygen with electrodes fabricated from this catalyzed substrate are obtained in 6M KOH under 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 -MnO₂ possesses the maximum catalytic activity (Brenet 1979; Trasatti 1980). Electrocatalytic activity of γ -MnO₂ towards oxygen reduction has been explained by Brenet (1979) in light of the redox couples (Mn⁴⁺/Mn³⁺) through the following mechanism:



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 -MnO₂ catalyst onto the coconutshell charcoal substrate and the electrochemical performance of the electrodes fabricated from such a substrate for dioxygen reduction in concentrated alkali.

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2. Experimental

2.1 Deposition of γ -MnO₂ onto the carbon substrate

The chemical method adopted to prepare γ -MnO₂ catalytic oxide is similar to that described by Gattow and Glemser (1961). KMnO₄ containing desired weight percent of MnO₂ 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 -MnO₂ onto the carbon substrate. Formation of γ -MnO₂ catalytic oxide was ascertained by x-ray powder diffraction. A diffused diffraction pattern characteristic of amorphous γ -MnO₂ was obtained (Zwicker *et al* 1962).

2.2 Preparation of the electrodes

Electrodes of various carbon specimens were prepared by hot pressing the γ -MnO₂ deposited carbon substrate at 140°C at an optimized pressure of 0.05 ton/cm² on expanded platinum metal screens with 20% polyethylene 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 -MnO₂, 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 -MnO₂ 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 -MnO₂ 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

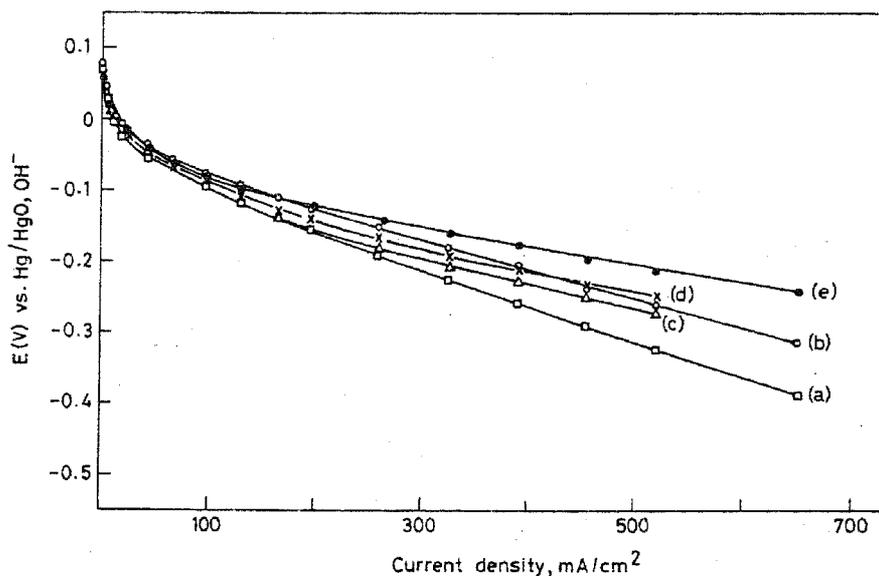


Figure 1. Current-potential curves for the electroreduction of dioxygen on (a) bare carbon electrode, (b) a 7 wt % Pt catalyzed carbon electrode, (c) a 8 wt % (d) a 4 wt % (e) a 2 wt % γ -MnO₂ catalyzed carbon electrode.

polarization components. The activity for dioxygen reduction on the carbon electrodes catalyzed with 2 wt % of γ -MnO₂ is competitive with the 7 wt % platinized carbon electrodes. The 2 wt % γ -MnO₂ catalyzed carbon electrode could be loaded with a current density of 650 mA/cm² at the polarization potential of -0.24 V vs Hg/HgO, OH⁻. To avoid the cathodic reduction of γ -MnO₂ catalyst (Sathyanarayana and Sridharan 1976) (which takes place at -0.3 V vs Hg/HgO, OH⁻) the electrodes were not subjected to polarization beyond this potential.

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