

Short communication

Nickel-modified manganese oxide as an active electrocatalyst for oxidation of methanol in fuel cells

Purnakala V. Samant, Julio B. Fernandes *

Department of Chemistry, Goa University, Taleigao Plateau, Goa 403206, India

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Abstract

Anodic oxidation of methanol is investigated in sulfuric acid electrolyte at 25° and 60°C on iron and nickel modified manganese oxide electrodes. The oxide layer is produced as a thin film in situ by thermal decomposition of the precursors on a platinum substrate. The electrochemical activity is investigated as a function of the nature of the dopant, the amount of dopant, and the effect of heat treatment of electrode strips. It is found that nickel modified manganese oxide is significantly active for the electro-oxidation of methanol. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Methanol electro-oxidation; Fuel cell; Electrocatalyst; Modified manganese oxide

1. Introduction

It has been proposed [1] that the direct methanol–air fuel cell (DMFC) is a promising power source for road transportation. Different catalysts for DMFC, have been studied, but platinum and platinum-group metals are found to be most successful [2,3]. Further, the electrochemical activity of carbon-supported platinum catalysts is known to increase in the presence of a second metal such as ruthenium, tin or tungsten, either as an alloy or a bimetal. This also serves to decrease the cost of the electrocatalyst [3,4]. Recently, a catalyst obtained by reduction of nickel tungstate has also been found to be active [5]. Finally, oxides and mixed oxides such as Fe, Sn, La, In, Pb and V have been examined as modifying materials for methanol oxidation. In the present investigation, modified manganese oxides are investigated as potential materials for the electrocatalytic oxidation of methanol.

2. Experimental

The thermal decomposition of catalyst precursors on a platinum substrate for all modifications was performed using the following procedure.

(i) An appropriate amount of metal nitrate or mixed metal nitrate in aqueous form was impregnated with a suitable oxidizing agent.

(ii) Thin layers of the above mixtures were applied to platinum foil.

(iii) The composites from (ii) were gradually dried in a furnace at different temperatures. A platinum plate of size 1 cm × 2.2 cm × 2.2 mm was used as the substrate. A solution of 0.1 M $\text{Mn}(\text{NO}_3)_2$ prepared in 0.1 M HNO_3 aqueous solution was applied to one side of the substrate in several successive coatings. After each coating, the solution was dried at a moderate temperature (100°C in oven), decomposed in a furnace at 170°C for 10 min, and finally heated to 450°C for 30 min. The geometric area exposed to the solution was 1 cm².

Nickel modified manganese oxide catalysts were prepared by taking an appropriate amount of nickel nitrate 0.1 M $\text{Mn}(\text{NO}_3)_2$ and sodium perchlorate and applying this mixed solution to a platinum substrate using the above procedure.

* Corresponding author. Tel.: +91-0083-221-346; E-mail: julio@unigoa.ernet.in

Electrochemical measurements were carried out in 2.5 M H_2SO_4 and 1 M CH_3OH . Graphite was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Steady-state potentiostat polarization curves were obtained for anodic oxidation of methanol at ambient temperature and 60°C.

3. Results and discussion

Polarization curves are presented in Figs. 1–5. Fig. 1 makes a comparative study of Fe^{3+} -doped and Ni^{2+} -doped manganese oxides for methanol oxidation at 25 and 60°C. At a current density of 100 mA cm^{-2} , it can be seen that the Ni^{2+} -doped manganese oxide has a superior electrocatalytic activity by 140 mV, i.e., it gives a higher current output at an overpotential which is 140 mV less than that of the Fe^{3+} -doped sample. Therefore, the nickel–manganese oxides were investigated further. The electrocatalytic activity is also dependent on the temperature at which the deposited electrodes are heat treated. Hence, they were subjected to heat treatment between 250 and

450°C. The activity was found to increase with increasing temperature. At a current output of 100 mA cm^{-2} , for example, the 450°C heated sample exhibits an overpotential which is 100 mV less than that for the 250°C heated sample, when a comparison is made between the potential curves at 60°C (Fig. 2). Heat treatment beyond 450°C cannot be undertaken since manganese oxides are known to undergo phase changes at such temperatures.

In order to elucidate the effect of the amount of Ni^{2+} in the manganese oxide, an investigation was performed by preparing manganese oxides which contained varying amounts of Ni^{2+} , viz., Ni:Mn compositions of 0.04:0.010, 0.04:0.013, and 0.04:0.020. The polarization curves for the samples are given in Fig. 3. The samples with 0.04:0.013 Ni:Mn display better characteristics than the 0.04:0.010 or 0.04:0.020 samples. Thus, an optimum amount of Ni^{2+} in manganese oxide is desirable. A comparison of the curves at 60°C (current = 100 mA cm^{-2}) for the 0.04:0.010 and 0.04:0.013 samples shows that the overpotential of the latter sample is lower by 225 mV, for the 0.04:0.013 and 0.04:0.020 samples, the overpotential of latter is less by 20 mV.

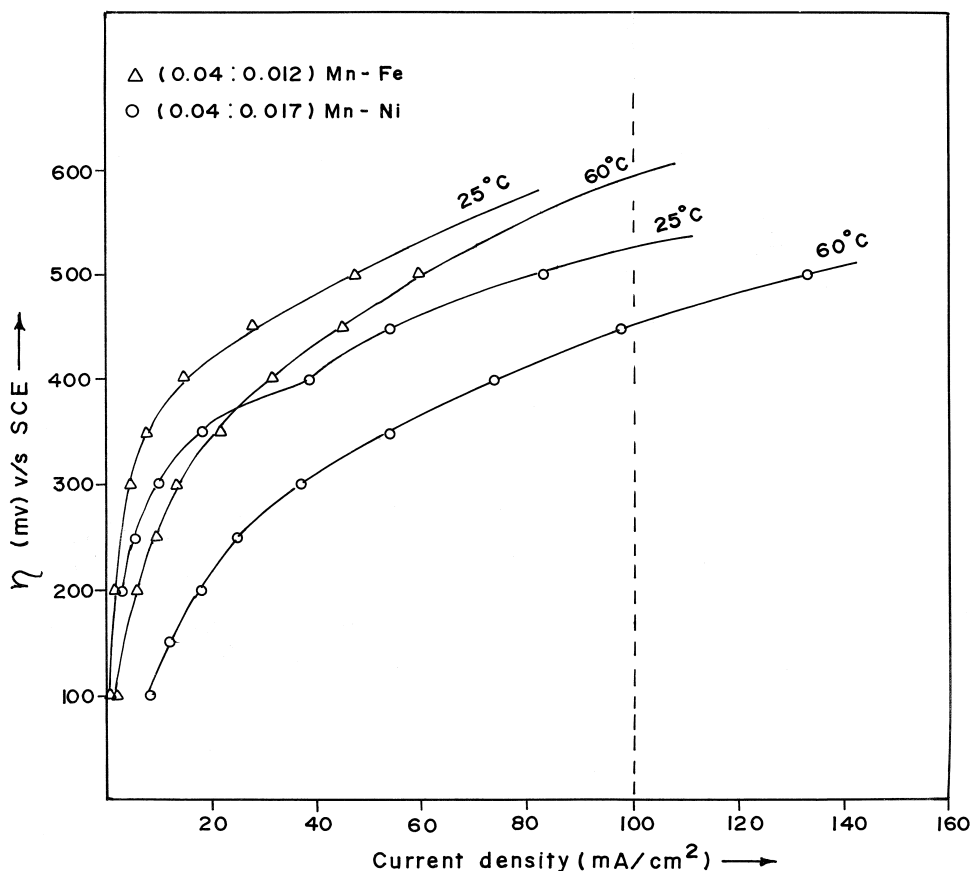


Fig. 1. Polarization curves (2.5 M H_2SO_4 , 1 M CH_3OH) for electro-oxidation of methanol on modified manganese dioxide electrodes at 25 and 60°C. (Δ) Mn–Fe; (\circ) Mn–Ni.

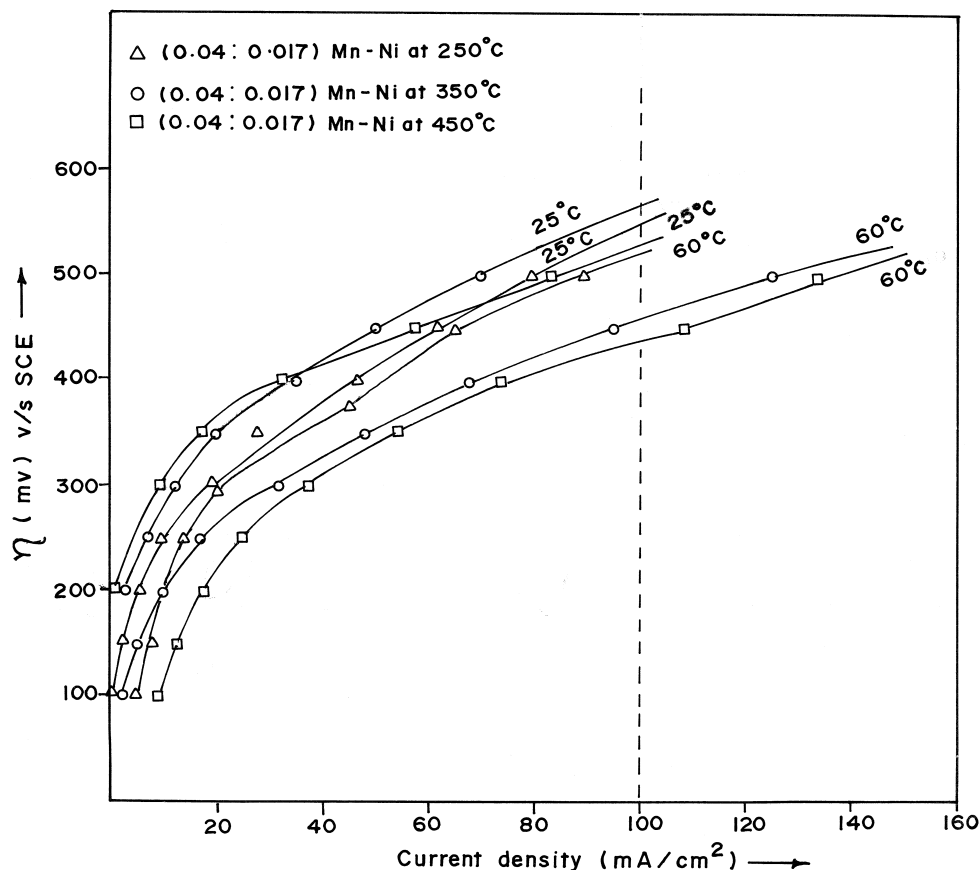


Fig. 2. Polarization curves (2.5 M H_2SO_4 , 1 M CH_3OH) for electro-oxidation of methanol on modified manganese dioxide electrodes at 25 and 60°C as a function of the temperature of heat treatment (250, 350 and 450°C, as indicated).

A comparative study of the Tafel plots of Fe^{3+} -doped and Ni^{2+} -doped manganese oxides of composition 0.04:0.012 Mn–Fe and 0.04:0.017 Mn–Ni is given in Fig. 4. The data are in agreement with the above observations that Ni^{2+} -doped samples are superior to Fe^{2+} -doped samples as the latter have a significantly higher overpotential at low current density.

Tafel plots for various Ni^{2+} -doped manganese dioxides (0.04:0.010, 0.04:0.013, 0.04:0.020 Mn:Ni) are given in Fig. 5. The Tafel slopes of the various plots are all around 180 mV, i.e., about twice that reported for conventional platinum-based electrocatalysts (~ 95 mV) for the electro-oxidation of methanol. The magnitude of the Tafel slope is known to depend on the electrocatalytic reaction mechanism and the adsorbed states of methanol and its decomposition products. We therefore predict that new type of mechanism is occurring on the modified manganese dioxide electrodes. In fact, in a recent investigation of Pt– WO_3 electrodes for methanol electro-oxidation, Hamnett et al. [6] predicted an oxyhydroxide surface structure which can be associated with proton insertion. Manganese dioxide is a well known proton insertion electrode [7–10] and has an active hydroxylated surface. Preliminary

experiments with Ni^{2+} -doped manganese oxide samples, indicated a rich hydroxylated surface. We therefore suggest simultaneous proton–electron intercalation of the nickel–manganese electrode which favours the electro-oxidation of methanol. Further investigation of this concept is in progress.

4. Conclusions

- (1) A new Ni^{2+} -modified manganese oxide electrode has been investigated for the first time, for the anodic oxidation of methanol.
- (2) The Ni^{2+} -modified electrode is quite active for methanol oxidation. By contrast, the Fe^{3+} -modified oxide exhibited poor electrocatalytic activity.
- (3) The activity of Ni^{2+} -modified electrodes is dependent on: (i) the temperature of the thermal treatment of electrodes; (ii) the amount of Ni^{2+} in the electrode; and (iii) the nature of dopant.
- (4) The anodic oxidation of methanol on oxide intercalation electrodes, such as modified manganese dioxide, is

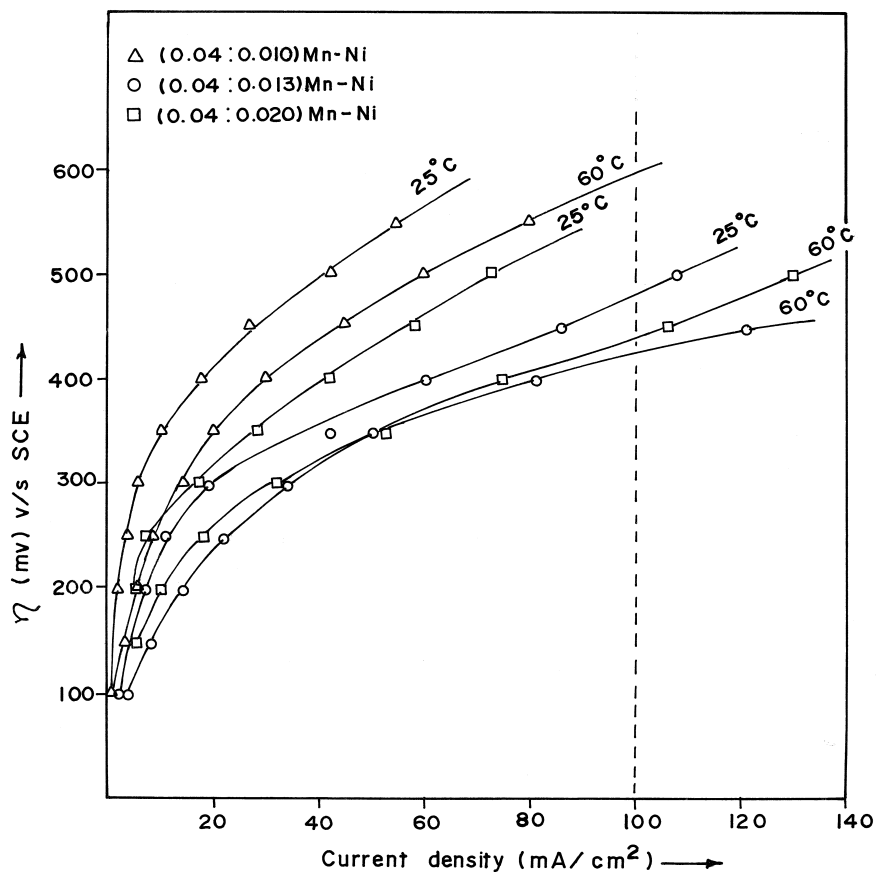


Fig. 3. Polarization curves (2.5 M H_2SO_4 , 1 M CH_3OH) for electro-oxidation of methanol on modified manganese dioxide electrodes at 25 and 60°C as a function of molar composition of Ni^{2+} .

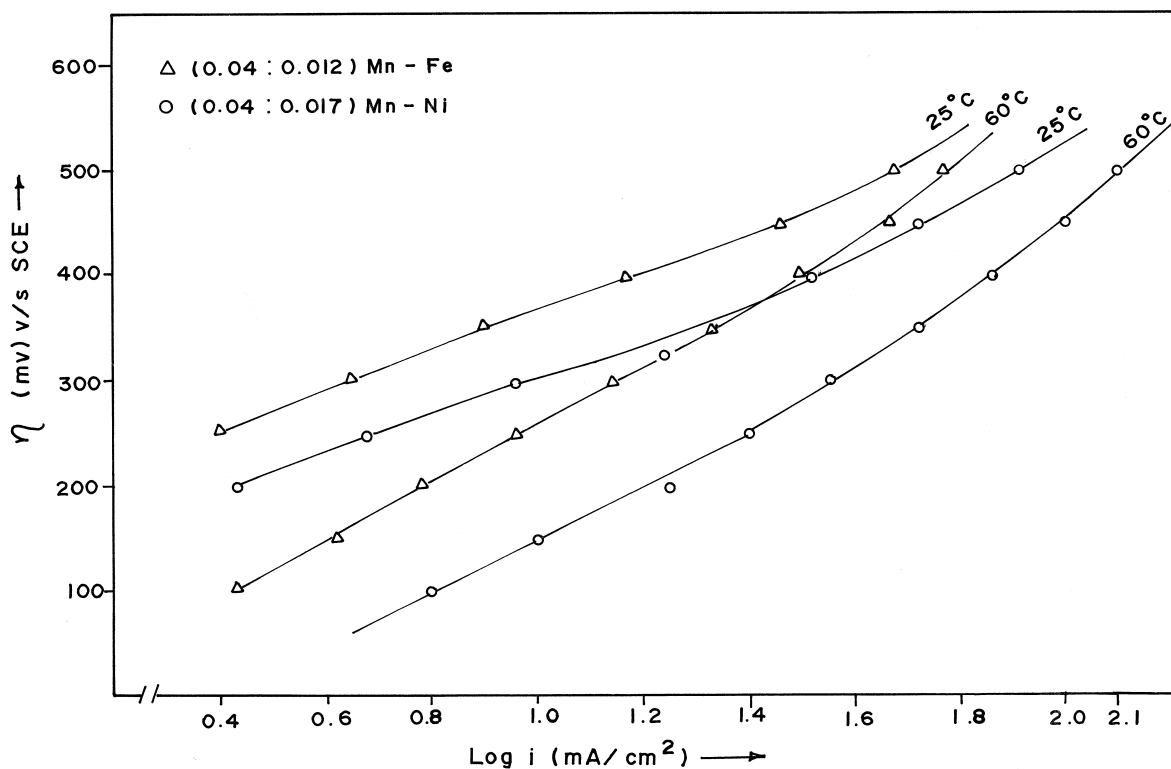


Fig. 4. Tafel plots (2.5 M H_2SO_4 , 1 M CH_3OH) of Fe^{3+} -doped and Ni^{2+} -doped manganese dioxide.

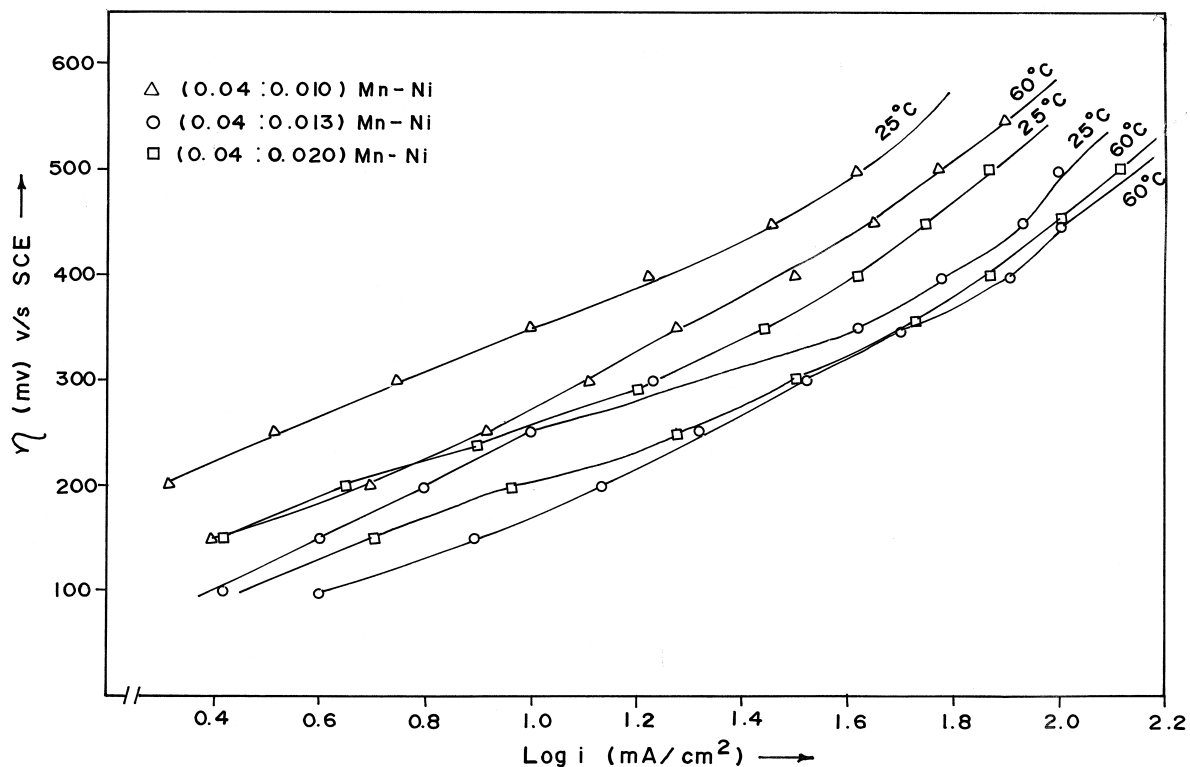


Fig. 5. Tafel plots (2.5 M H₂SO₄, 1 M CH₃OH) of manganese dioxides containing varying amounts of Ni²⁺.

believed to follow a mechanism, which is different from that on conventional platinum-based electrodes.

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