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Electrodeposited MnO_2 as electrocatalyst for carbohydrate oxidation

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Abstract

The electrochemical oxidation of dextrose, fructose and sorbitol under galvanostatic conditions was carried out using both anodically and cathodically deposited MnO_2 layers on platinum and carbon. The coated electrodes showed better electrocatalytic activity for the oxidation of carbohydrates than the bare substrates. Catalytic participation of some higher valent states of manganese in electron transfer relay is speculated, which finds support in the chronopotentiogram and the observed pH-dependence of the electrochemical parameters. The current potential plots showed Tafel behaviour for the MnO_2/Pt electrode. The Tafel slopes were found to be relatively high, indicating kinetic complications. The observed unusual negative values of electrochemical reaction order on MnO_2/Pt electrode were accounted for by considering slow desorption of oxidation products from the electrode surface. The adsorption isotherms of dextrose and fructose on MnO_2 were determined. The current efficiencies of oxidation of carbonyl and hydroxyl groups were found to be ~ 40 and $\sim 50\%$ respectively. SEM pictures showed the cathodically deposited MnO_2 on carbon to be more fine-grained and smoother than the corresponding anodic deposits.

1. Introduction

Direct methanol fuel cells (DMFC) are at present close to commercial reality [1–3]. A large number of studies on the electro-oxidation of other alcohols, particularly ethanol, have also been carried out [4–17]. However, the promising electrocatalysts developed so far for oxidation of alcohols are almost invariably expensive noble metals and their composites supported on various substrates.

Carbohydrates can be considered to be potentially useful in fuel cell application [18] due to the presence of the oxidisable carbonyl group in the molecule, along with the multiple hydroxyl groups. Moreover, the relative abundance of the most important monosaccharide, dextrose, is so high that it has been estimated that there are more dextrose units in nature than the total number of all other organic groups [19]. The main problem is to find an efficient and acceptable electrocatalyst for such an oxidation. The concept of biofuel cells has been proposed and tested by using suitable enzyme electrodes for dextrose oxidation [20–22]. However, such electrodes have a limitation in the sense that they are usually degraded under harsh experimental environments such as high acidity, alkalinity, ionic strength and temperature.

The non-enzymatic electrochemical oxidation of carbohydrates, particularly dextrose, has been studied from the point of view of analytical applications. The materials used for this purpose include bulk metals (Au, Pt) with different surface treatments [23–26], metal (Pt, Cu) alloys [18, 27], microparticles of metals (Pt, Au, Cu) dispersed on different substrates or incorporated into polymeric matrices [28–32], metal (Ni, W, Ru) oxides [33–35], metal (Ru) complex [36] and different types of carbon based electrodes [32, 37–39]. However, to qualify as an electrocatalyst for fuel oxidation the electrochemical response needs to remain stable over a considerable period of time. In the present work we have used MnO_2 deposits on platinum and carbon prepared electrochemically by both anodic [40] and cathodic routes. Our findings on the characteristics of the steady state oxidation of dextrose, fructose and sorbitol on these electrodes are reported here.

2. Experimental

A platinum (Pt) wire electrode and the flat surface of a cylindrical carbon (C) rod used in dry cells were taken as supports for the MnO_2 layers. Anodic and cathodic deposits of MnO_2 were prepared from 1 M $MnSO_4$ and 0.1 M $KMnO_4$ solutions respectively using current densities of 3–8 mA cm^{-2} and deposition time of 30–75 min. The composition of the deposits were verified by measuring the potentials of the deposited electrode in solutions with different concentrations of Mn^{+2} and of different pH maintained by acetic acid–acetate buffer. The observed dependence of electrode potential on pH and Mn^{+2} concentration was found to fairly agree with the following redox process

$$MnO_2 + 4H^+ + 2e \rightarrow Mn^{+2} + 2H_2O$$

The standard electrode potentials were calculated to be 1.30 V (anodic MnO_2/Pt), 1.30 V (cathodic MnO_2/Pt), 1.20 V (anodic MnO_2/C), 1.29 V (cathodic MnO_2/C) against the literature value of 1.23 V vs. RHE [41].

Steady state potentials for oxidation of dextrose, fructose and sorbitol from solutions of different concentrations with 0.25 M Na_2SO_4 as the supporting electrolyte on MnO_2/Pt and MnO_2/C electrodes were determined at different applied current densities within the range 0.08–1.3 mA cm^{-2} by using a constant current source (DB-300, DB Electronics, India) and a digital multimeter (DM 6104B, ECIL, India). Chronopotentiograms were recorded by using Ministat (AEW2-10, Sycopel Scientific Ltd., U.K.). Potentials reported were measured with respect to a saturated calomel electrode (SCE).

Adsorption of dextrose and fructose on MnO_2 powder was studied by equilibrating known volumes of 0.01–1 M carbohydrate solutions with known amounts of the solid and estimating the equilibrium concentration by Fehling's solution titration [42]. The same analytical technique was used to determine the concentration of the carbonyl groups before and after prolonged electrolysis of dextrose, fructose, sorbitol and glycerol solutions on an anodically deposited MnO_2 electrode with a Pt wire mesh of sufficiently large surface area as the base. The current efficiencies for the respective oxidations were calculated from the results.

Electrode surface microstructures were examined with the help of a scanning electron microscope (JSM 5200, Mic JEOL, Japan). The chemicals used were of AR grade. All the experiments were carried out at room temperature (30 ± 2 °C).

3. Results and discussion

3.1. *Comparison between the bare substrates and the MnO_2 deposited ones*

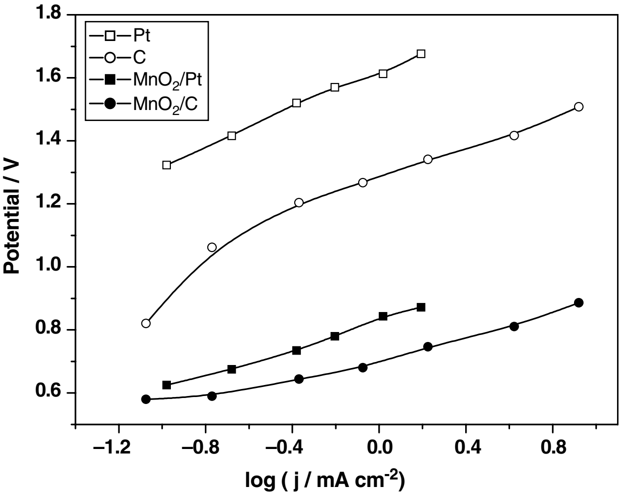

Fig. 1. Plots of steady state potential (vs. SCE) vs. log current density for oxidation of dextrose from 1 M solution on Pt, C, MnO_2/Pt and MnO_2/C electrodes.

Galvanostatic current–potential measurements (Figure 1) show that the steady state potential for dextrose oxidation at a fixed current density is less positive on anodically deposited MnO_2 layers on platinum (Pt) and carbon (C) than the corresponding values on bare substrates. This observation primarily indicates that modifying the electrode surface with an MnO_2 deposit facilitates the oxidation of dextrose. The enhancement of oxidation kinetics by the oxide layer can be rationalized as a combined effect of two factors. Firstly, dextrose is expected to be adsorbed quite easily on MnO_2 due to the possibility of hydrogen bond formation using the multiple hydroxyl groups present in the molecule. Secondly, the electron transfer mechanism may involve the participation of some intermediate manganese species with an oxidation state of other than + 4, which is continuously generated and consumed during the oxidation process. Hence the electro-oxidation of dextrose on MnO_2 can be considered to be a mediated electron transfer, MnO_2 acting not only as a simple electron sink but also as a catalyst. Chronopotentiograms for dextrose oxidation (Figure 2) clearly demonstrate this point. On MnO_2/Pt, even in the absence of dextrose, a chronopotentiometric response is obtained. In the presence of dextrose the transition time for this response is found to increase considerably, though the potentials remain more or less the same. This is characteristic of a catalytic EC mechanism [43] where the primary electrochemical process appears to be the generation of some higher-valent manganese species,

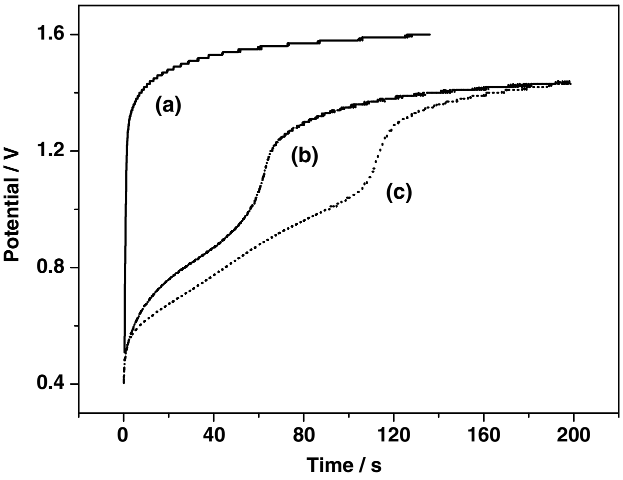

Fig. 2. Anodic chronopotentiograms at 2.0 mA cm^{-2} on (a) Pt (10 mM dextrose), (b) MnO_2/Pt (in absence of dextrose) and (c) MnO_2/Pt (10 mM dextrose).

which are subsequently consumed by oxidising dextrose. By contrast, dextrose oxidation does not take place on Pt as the potential is found to move quickly to the oxygen evolution region.

Experiments were also carried out in alkaline medium to investigate the effect of pH on the oxidation process. As the oxidation of the aldehyde or the hydroxyl group in dextrose requires simultaneous release of H^+ ions and electrons, the process should be favoured thermodynamically by increase in the alkalinity of the medium. This expectation is realized in the case of bare Pt and C electrodes. The steady state potentials at fixed current densities were found to be shifted towards considerably less positive values in alkaline medium. By contrast, it was observed that such shifts become significantly smaller on MnO_2/Pt and MnO_2/C electrodes. This is demonstrated by the plots of the difference (ΔE) between the steady state potentials in neutral and in alkaline media on both bare and MnO_2 coated Pt and C electrodes (Figure 3). This observation further supports the earlier supposition regarding the mechanism of the catalytic role of MnO_2 in the oxidation process because all the oxo-manganese species like MnO_2, MnO_3^-, MnO_4^- etc are expected to become thermodynamically less powerful oxidants with decrease in H^+ ion concentration.

3.2. *Explanation of the electrochemical reaction order*

The electrochemical reaction orders for oxidation of different molecules on anodically prepared MnO_2/Pt electrodes were determined from the slopes of the log current vs. log concentration plots at constant potential. These are presented in Table 1 for dextrose and fructose along with some other alcohols containing varying number of hydroxyl groups. The reaction orders are found to be negative for the carbohydrates and positive for the alcohols. This unusual behaviour of the former can be rationalized by considering slow desorption of the oxidation product from the electrode surface. The adsorption of the molecules in the present study on the oxide surface is likely to occur via hydrogen bonding with the hydroxyl groups. Also, unless the adsorbed oxidation product is desorbed sufficiently fast, a part of the electrode surface may remain unavailable for the oxidation to continue. Indeed, the formation of a passive film on boron-doped diamond by adsorption of the oxidised dextrose molecules onto the electrode surface has been reported [38]. Thus with increasing coverage of the electrode surface by the oxidation product the true current density is expected to be progressively higher than the apparent current density measured on the basis of the availability of the full geometrical area. The product desorption step is likely to become gradually slower with increasing number of hydroxyl groups in the molecule as the ability to form hydrogen bonds with the surface is retained even after the oxidation of a single carbonyl or hydroxyl group. This is demonstrated by the changeover of the electrochemical reaction order from a negative to a positive value with decreasing number of hydroxyl groups in the series of molecules studied (Table 1).

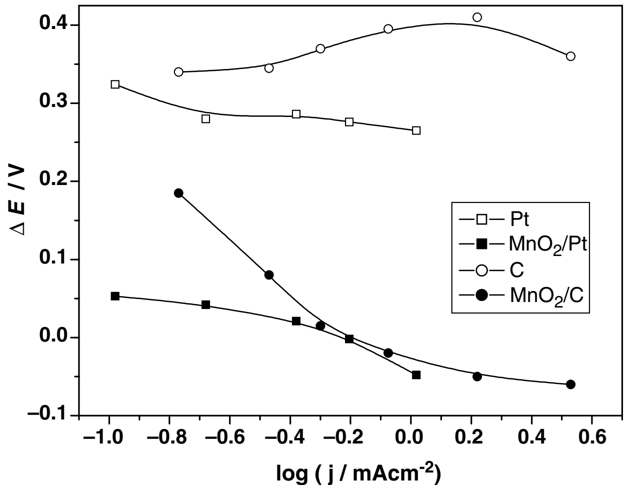

Fig. 3. Plots of the difference (ΔE) between the steady state potentials in neutral and in alkaline media vs. log current density for oxidation of dextrose from 1 M solution on Pt, C, MnO_2/Pt and MnO_2/C electrodes. [10^{-3}M NaOH for Pt; 10^{-2}M NaOH for C].

The above explanation can be justified by the following semi-quantitative treatment. Let j and j^* denote the measured and the true current densities respectively and θ be the fractional coverage. Then, one can write

$$j = (1-\theta)j^* = (1-\theta)nFk^*c_s\exp(\alpha_a nFE/RT) \tag{1}$$

where n, α_a, k^*, c_s and E denote the number of electrons transferred, the transfer coefficient, the potential independent rate constant, the surface concentration of the molecule being oxidized and the steady state potential respectively. Assuming the Langmuir isotherm for reactant adsorption, as well as the equality of the rates of accumulation and desorption of the oxidation product under the steady state, the following equations can also be written.

$$c_s = Ac(1+Bc)^{-1} \tag{2}$$

and

$$k_a j^* = k_d\theta \tag{3}$$

where c is the bulk concentration and A, B, k_a and k_d are the appropriate constants. Hence, the electrochemical

Table 1. Electrochemical reaction order (ρ) for oxidation of different molecules on anodically prepared MnO_2/Pt

Molecule	ρ
Dextrose	−0.39
Fructose	−0.11
Sorbitol	−0.01
Glycerol	0.13
Propane-1,2-diol	0.35
Ethylene glycol	0.28
Ethanol	0.65
Methanol	0.55

reaction order (ρ) can be obtained by combining Equations 1, 2 and 3 and is given by

$$\rho = [\delta \log j/\delta \log c]_E = [1 - \theta/(1-\theta)](1 + Bc)^{-1} \quad (4)$$

Thus ρ becomes negative when $\theta > 0.5$

Adsorption of dextrose and fructose on MnO_2 powder was studied considering the Langmuir monolayer adsorption model to be applicable. The relevant equation is

$$w = (a_0/a)Kc(1 + Kc)^{-1} \quad (5)$$

where w is the mass of the carbohydrate adsorbed per unit mass of MnO_2, a_0 the surface area per unit mass of MnO_2, a the area covered by unit mass of the carbohydrate and K the adsorption equilibrium constant. The higher values of (a/a_0) and K obtained for dextrose (12.1 and 37.5 M^{-1} respectively) compared to those for fructose (5.2 and 6.7 M^{-1} respectively) indicate that the former is adsorbed more strongly covering a larger surface area than the latter. It can be argued that the relative order of the extents of adsorption would remain the same for both the parent carbohydrate molecules and their respective oxidation products because the oxidation of the carbonyl groups leaves the number of hydroxyl groups unchanged. This assumption accounts for the observed less negative reaction order for fructose than in case of dextrose because, by Equation 4, increasing the value of the fractional surface coverage θ beyond 0.5 is expected to make ρ more negative.

3.3. *Current efficiency of oxidation*

The current efficiencies of oxidation of dextrose and fructose were estimated on the basis of the decrease of carbonyl groups on prolonged electrolysis, as determined from titration with Fehling's solution. The efficiency obtained was around ~40% for both dextrose and fructose assuming two-electron oxidation of the carbonyl groups. However, if the hydroxyl groups present are also oxidized to carbonyl groups then the net decrease of carbonyl groups should be less than the expected amount and hence the above figure for current efficiency is likely to be an underestimate. To explore this point the current efficiencies

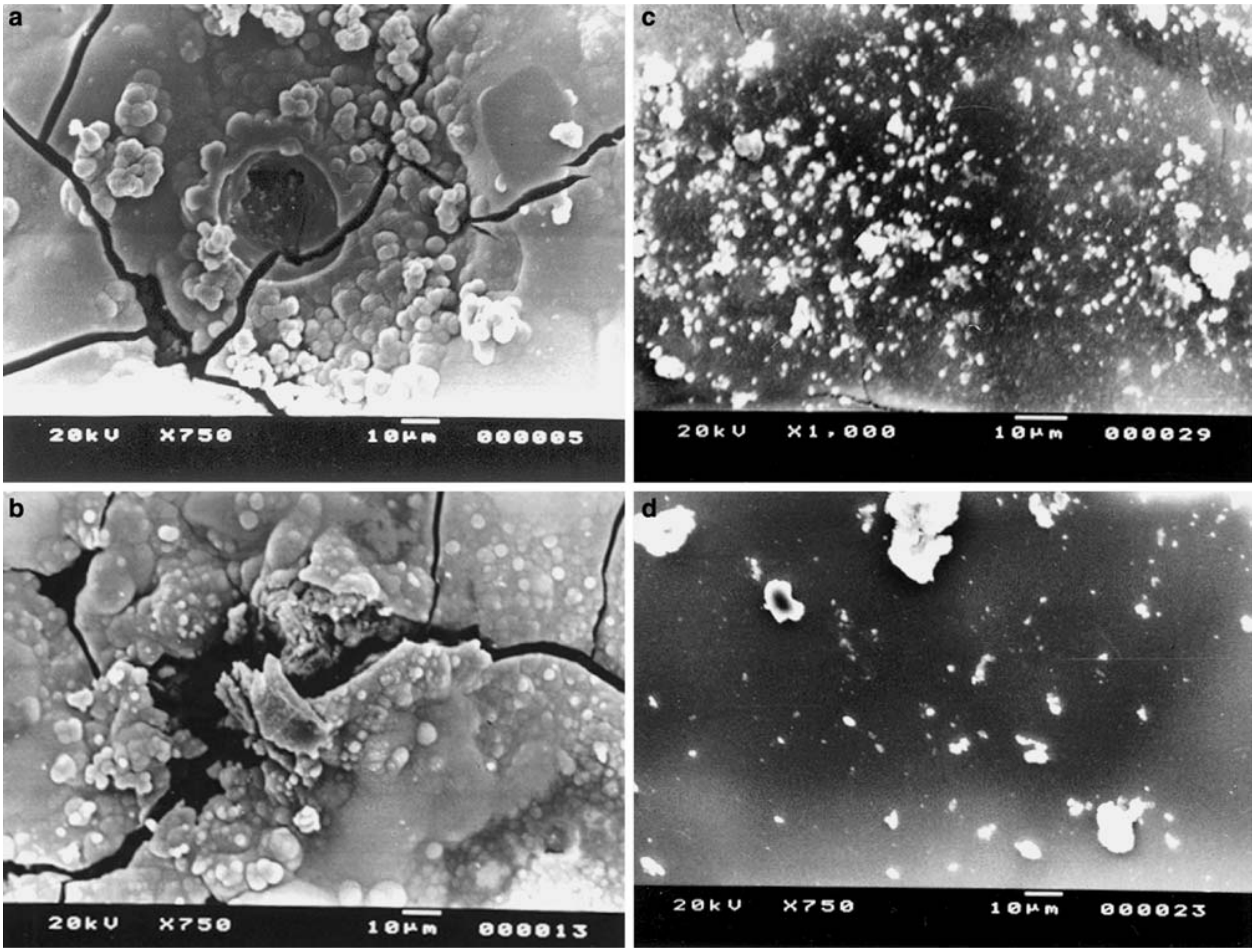

Fig. 4. SEM photographs of different electrode surfaces (a) MnO_2/C (anodic deposit) (b) MnO_2/C (anodic deposit after anodic pre-electrolysis in 0.25 M Na_2SO_4) (c) MnO_2/C (cathodic deposit) and (d) MnO_2/C (cathodic deposit after anodic pre-electrolysis in 0.25 M Na_2SO_4).

of oxidation of the hydroxyl groups in sorbitol and glycerol in terms of the increase of carbonyl groups were also determined by the same technique and these were found to be around ~ 50%. Though the oxidation of the carbonyl groups in aldehydes and α-hydroxy ketones is energetically easier than that of the hydroxyl group, the latter oxidation may be statistically more likely in a carbohydrate molecule. The maximum current efficiency achievable for total oxidation can, therefore, be calculated as a sum of the above two efficiencies, i.e., around ~ 90%.

3.4. *Comparison between anodic and cathodic deposits*

MnO_2 can also be deposited cathodically from MnO_4^- solution. When such cathodic deposits were used for oxidation of the carbohydrate molecules the attainment of steady state potential at a fixed current was found to require quite a long period. The drift of potential towards the steady state value started from a considerably less positive value. This behaviour can be effectively suppressed by anodic pre-electrolysis for some time in the supporting electrolyte before adding the carbohydrate, while such pre-electrolysis was found to have little effect on the behaviour of anodically deposited MnO_2. The scanning electron microscopic pictures of anodic and cathodic electrodeposits of MnO_2 on carbon are shown in Figure 4. While the anodic deposit was found to be coarse grained with average grain size of ~2–5 μm, the cathodic deposit appeared to be smoother but strewn with islands of fine grains of possibly a second solid phase. The surface density of this phase was found to decrease significantly after pre-electrolysis in the supporting electrolyte, while the nature of the anodic deposit remained more or less unchanged by this treatment (Figure 4). Thus it seems more likely that during the cathodic deposition some other reduced species in addition to MnO_2 are formed, which get oxidized initially.

3.5. *Steady state current potential characteristics*

Figure 5a, b and c show the steady state potential vs. log current density plots for oxidation of dextrose, fructose and sorbitol respectively on anodic and cathodic deposits of MnO_2 with both Pt and C supports. These can be considered to reflect the expected long time performance of the electrodes. Measurements on the cathodic deposits were carried out after anodic pre-electrolysis in the supporting electrolyte for the reason already given (Section 3.4). The plots were found to be fairly linear on MnO_2/Pt electrodes showing Tafel behaviour with slopes of around ~ 0.2 V. Relatively high values of the Tafel slopes possibly indicate kinetic complications due to slow product desorption as discussed earlier (Section 3.2). However, on MnO_2/C the plots deviated significantly from linearity although the potentials were less positive than the corresponding values on MnO_2/Pt under similar current densities. The latter observation indicated that the electrocatalytic activity of the deposited MnO_2 layer increased on replacing Pt by C as the substrate. The steady state potentials were always found to be more positive for sorbitol than either fructose or dextrose on both MnO_2/Pt and MnO_2/C. As the reversible potentials of the corresponding oxidation processes are not experimentally obtainable, the overpotential generated cannot be computed. But phenom-

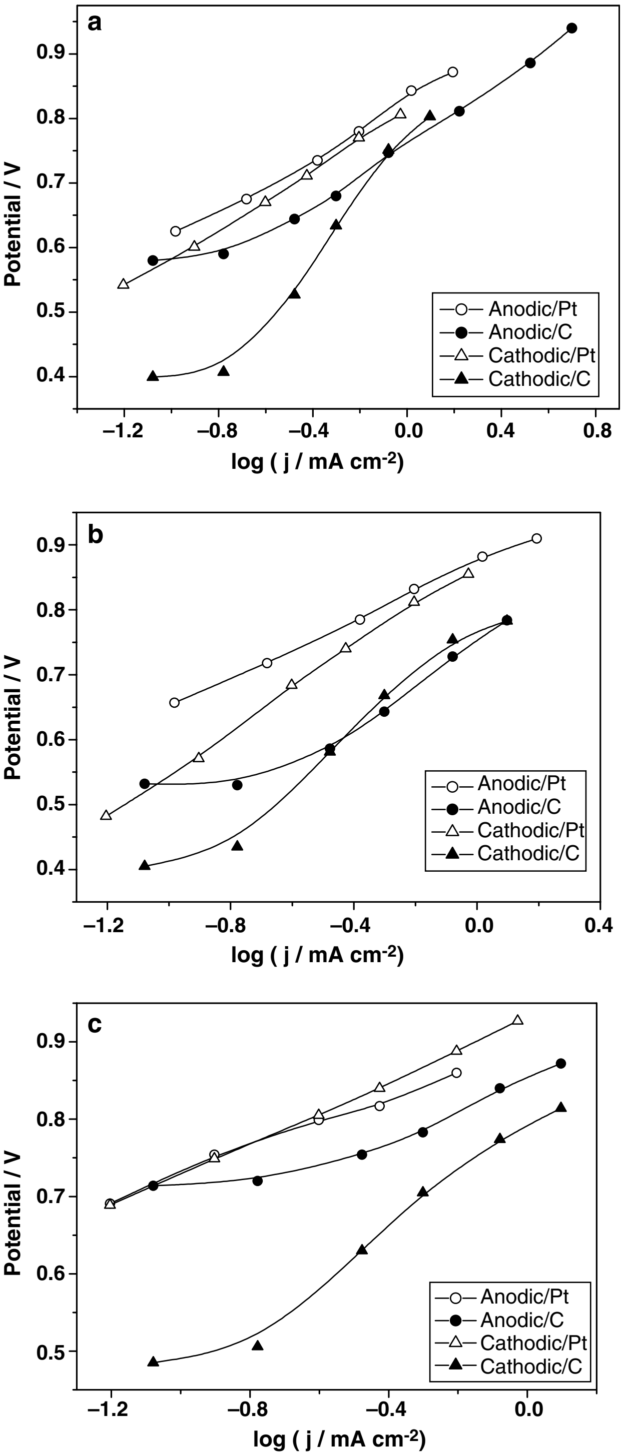

Fig. 5. Plots of steady state potential (vs. SCE) vs. log current density for oxidation of (a) dextrose, (b) fructose and (c) sorbitol from 1 M solution on anodic and cathodic deposits of MnO_2 on Pt and C.

enologically it can be concluded that the oxidation of sorbitol is more difficult than that of either dextrose or fructose. No clear-cut conclusion can be reached regarding the relative ease of oxidation between dextrose and fructose as the current–potential plots for these two showed a tendency to intersect. Similar comparisons also showed that while the ease of oxidation of all the molecules remained more or less equal on both anodic and cathodic deposits of MnO_2 on Pt, in the case of C support the cathodic deposit appeared to be a better electrocatalyst than the anodic deposit particularly at lower current densities. However, it is to be noted that the cathodic deposit requires higher charge input than that needed for an equivalent amount of anodic deposit because the change in the oxidation number of Mn during electrodeposition is greater in the former case.

4. Conclusion

The possibility of using both anodically and cathodically prepared MnO_2 as an electrocatalyst for oxidation of dextrose, fructose and sorbitol has been explored. It appears that the electrocatalytic activity of the material involves cycling between two oxidation states of Mn. Though a current efficiency of $\sim 90\%$ can be attained, the oxidation kinetics are controlled by the slow desorption of the product from the electrode surface. The results obtained show the efficacy of the material as electrocatalyst to be higher when deposited on carbon than on an expensive substrate like platinum. However, to be practically useful as a carbohydrate fuel cell anode material, the overpotential has to be lowered considerably. Whether this can be achieved by altering the deposition technique and other conditions will be the subject of our future work.

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