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Electrogeneration of Mn(III) in an undivided cell

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The electrochemical oxidation of manganous ion to manganic ion in acetic acid may be efficiently carried out in a parallel plate undivided cell. Reduction of manganic ion to manganous ion at the cathode is a relatively inefficient reaction, allowing the formation of solutions of manganic ion as high as 0.05 mol dm^{-3}, at greater than 80% current efficiency. The effects of the major variables have been evaluated.

1. Introduction

Manganic ion (Mn^{+3}) is a versatile oxidant used in a variety of organic syntheses [1–31] such as aromatic side chain oxidations, acetoxylations, amine oxidations, ketone oxidations, and phenol oxidation. Manganic salts are not readily available in large quantities but may be prepared chemically [32] or electrochemically [33, 34], from manganous (Mn^{+2}) salts. The electrochemical preparation of Mn^{+3} from Mn^{+2} in some cases may be carried out in the same medium as the organic reaction so that a regenerative or mediated reaction is performed [35, 36]. That is, the Mn^{+3} is formed over and over again from its reaction product Mn^{+2} so that a relatively small amount of manganese salt is required.

Although the literature contains a number of references to electrochemical generation of Mn^{+3}, we were unable to find a description of a simple inexpensive process for electrochemical generation. This report describes the electrochemical generation of Mn^{+3} from Mn^{+2} in acetic acid in an undivided cell.

2. Experimental procedure

The electrolysis system consisted of a reservoir, pump and cell. The reservoir was a 3 dm^3 round bottomed flask fitted with a heating mantle, thermometer, condenser, N_2 inlet, and solution entrance and exit lines. The connection to the pump was made via a 1/2″ (1″ = 2.54 cm) O.D. Teflon® tube. The pump was a centrifugal pump (March Mfg. Inc. Model MDX-XT-3) with Ryton® head, magnetically coupled Ryton® impeller and ceramic impeller shaft. Polypropylene connectors were used through the system. The cell (Fig. 1) consisted of two 1″ x 12″ graphite electrodes (Union Carbide AGSX) mounted in polypropylene blocks held together by 1/4″ thick aluminum backing plates and 1/4″ bolts. A butyl rubber gasket (1/16″ thick) was used between the polypropylene blocks. Entrance and exit ports were machined into the polypropylene blocks. Electrode contacts to the graphite were made through fittings in the polypropylene blocks with 1/4″ zirconium rods which were threaded and screwed into appropriate tapped holes in the graphite electrodes. The gap between electrodes was 3 mm. The pump forced 10 dm^3 min^{-1} of solution through the cell. It is important to note that the only relatively inexpensive metal we found to be stable in acetic acid solutions containing Mn^{+3} was zirconium.

In the experiment involving a Zr cathode, heavy Zr foil was attached to one of the graphite blocks with four Teflon® screws.

Samples of the electrolysis solution were removed during an experiment from the reservoir with a glass 2 cm^3 syringe via a 1/16″ bore Teflon® tube.

Gas sample were obtained from above the solution several times during an experiment and analysed for H_2, N_2, CH_4, C_2H_6 and CO_2 by gas chromatography.

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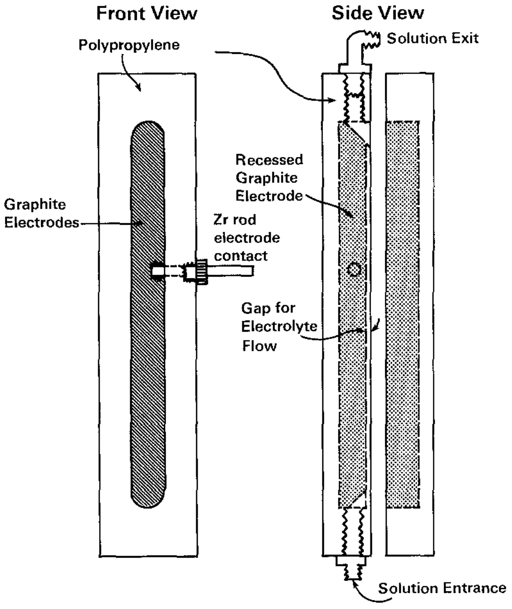

Fig. 1. Electrolysis cell.

The typical electrolysis solution consisted of 2600 cm^3 acetic acid, 396 g of anhydrous potassium acetate and 132 g of manganous acetate tetrahydrate. It was necessary to heat the solution to dissolve the salts.

The power supply used in all experiments was a Sorensen DCR 40-35A controlled current/voltage unit. Cell voltage was monitored with a Digitec Model 268 digital millivoltmeter.

The solutions were analysed for Mn^{+3} concentration by reacting the Mn^{+3} with KI and titration of the I_3^- with thiosulphate.

3. Results and discussion

Electrolyses of solutions of 0.17 mol dm^{-3} manganous acetate in acetic acid containing 1.28 mol dm^{-3} potassium acetate were carried out under a variety of conditions in an undivided parallel plate graphite electrode cell to determine the current efficiency for manganic ion production. One might expect that in an undivided cell the efficiency for manganic ion formation would be quite poor owing to reduction of the manganic ion at the cathode. It will be shown however, that under certain conditions, quite high current efficiencies may be obtained.

In these experiments the desired anodic reaction is oxidation of manganous ion to manganic ion. This appears to be the only anodic reaction as long as sufficient manganous ion is present at the anode to satisfy the current impressed. At high current densities it is possible to oxidize acetate leading to the formation of methane, ethane and CO_2.

The desired cathodic reaction is the reduction of protons to form hydrogen gas. If manganic ion is present it will also be reduced, forming manganous ion and resulting in a reduced overall current efficiency for manganic ion formation in the cell.

Figure 2 shows a plot of manganic ion concen-

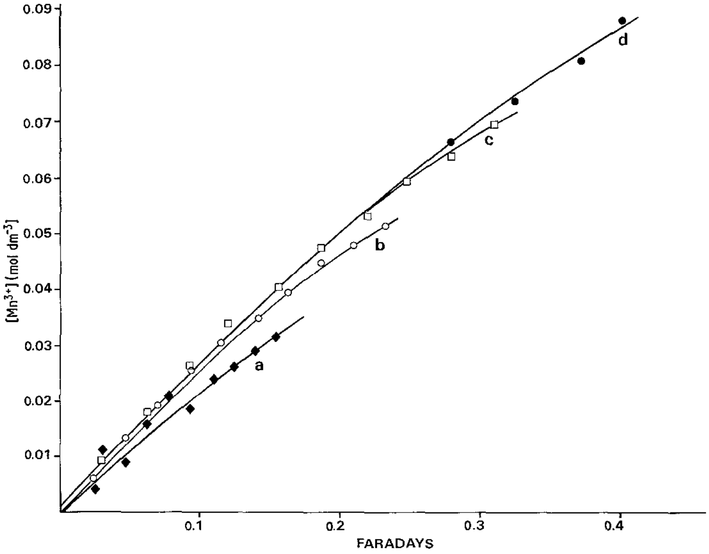

Fig. 2. Electrolysis carried out at 90°C. Current densities are, (a) 66 mA cm^{-2}; (b) 100 mA cm^{-2}; (c) 133 mA cm^{-2}; (d) 200 mA cm^{-2}.

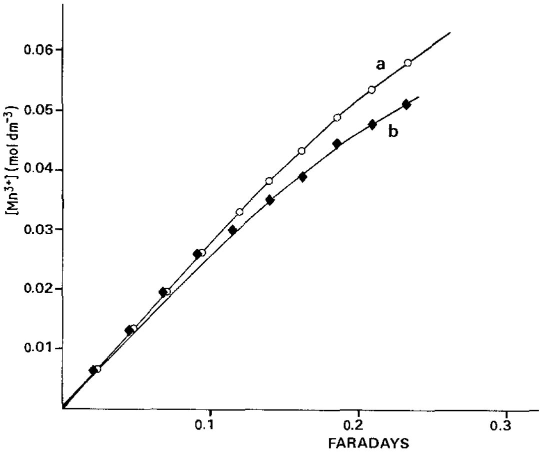

Fig. 3. Electrolyses at 100 mA cm^{-2} and (a) 70° C or (b) 90° C.

tration against Faradays of electricity passed through the cell for several current densities at 90° C. Note that current efficiency increases with increasing current density. The anodic reaction is quite selective for manganous ion oxidation except at 200 mA cm^{-2} when significant amounts of methane, ethane and CO_2 were formed via oxidation of acetate. The reduced current efficiency at lower current density suggests that the Mn^{+3} reduction is not a very rapid reaction, that is, it is not transport limited under these conditions.

The experiment at 133 mA cm^{-2} was repeated with sufficient acetic anhydride present to consume all the water added as the hydrate of manganous acetate. The plot of manganic ion concentration against Faradays of electricity passed was virtually the same as before.

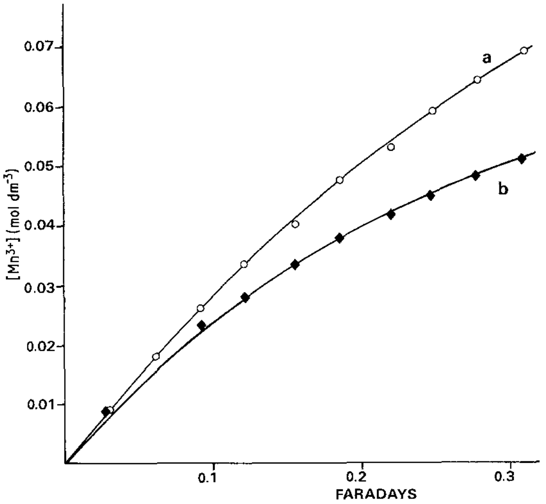

Fig. 4. Electrolyses at 132 mA cm^{-2} and (a) 90° C or (b) 110° C.

The effect of temperature on current efficiency is shown in Fig. 3 and 4. Part of the decreased current efficiency at higher temperature is a result of a higher rate of manganic ion loss to homogeneous oxidation of acetate. On standing at 90° C, the concentration of manganic ion in the above medium only decreased from 31.3 to 28.1 mmol dm^{-3} in one hour. Thus the main contribution to reduced current efficiency at higher temperature is probably an increased rate in the reduction of manganic ion.

Figure 5 is a plot of manganic ion concentration against Faradays of charge for two experiments identical except for flow rate through the cell. One reaction was carried out at the normal flow rate of 10 $dm^3 min^{-1}$, and the other at 1 $dm^3 min^{-1}$. The results were quite similar with only a slight decrease in current efficiency at the lower flow rate. Small amounts of methane and CO_2 were formed at the lower flow rate indicating that the current density exceeded that which could be satisfied by manganous ion transport to the anode.

The effect of reducing the manganous acetate concentration from 0.17 mol dm^{-3} to 0.08 mol dm^{-3} is shown in Fig. 6. In the reaction with only 0.08 mol dm^{-3} manganous acetate there was insufficient manganous ion to satisfy the 100 mA cm^{-2} current density at the anode resulting in considerable acetate oxidation to form methane, ethane and CO_2.

The concentration of electrolyte (potassium acetate) was high (1.28 mol dm^{-3}) in these

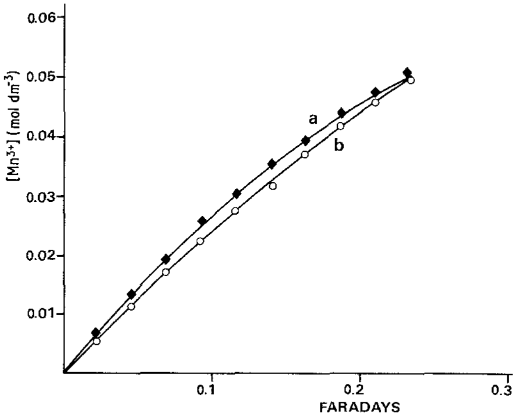

Fig. 5. Electrolyses at 100 mA cm^{-2}, 90° C and a flow rate of (a) 10 $dm^3 min^{-1}$ or (b) 1 $dm^3 min^{-1}$.

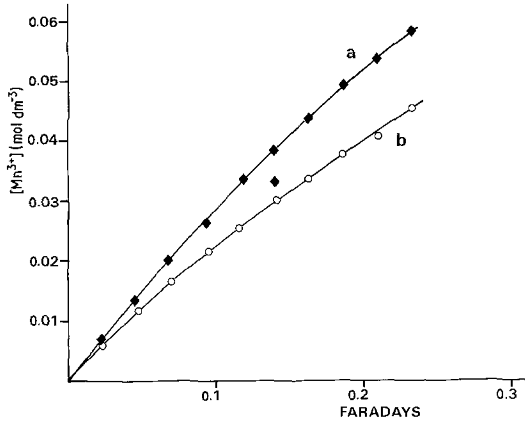

Fig. 6. Electrolyses at 100 mA cm^{-2}, 70° C and (a) 0.17 mol dm^{-3} manganous acetate or (b) 0.08 mol dm^{-3} manganous acetate.

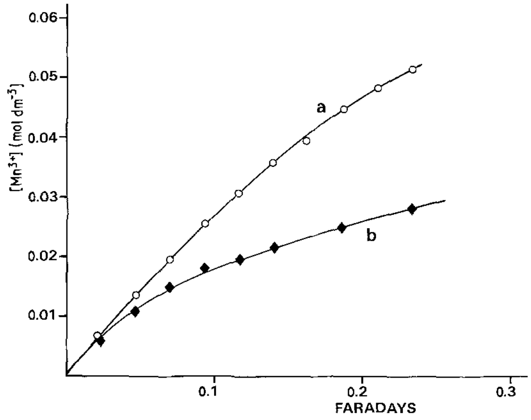

Fig. 7. Electrolyses at 100 mA cm^{-2}, 90° C and (a) 1.28 mol dm^{-3} potassium acetate or (b) 0.128 mol dm^{-3} potassium acetate.

reactions but the effect of a significant reduction in electrolyte concentration (to 0.128 mol dm^{-3}) was a drastic reduction in current efficiency as is shown in Fig. 7. There was also a great increase in cell voltage (4.6 V for the 1.28 mol dm^{-3} solution and 28 V for the 0.128 mol dm^{-3} solution) in the low electrolyte concentration experiment. The reduced cell current efficiency was not a result of poor efficiency at the anode as indicated by the absence of methane, ethane and CO_2. It seems likely that at the lower electrolyte concentration, the manganic ion must carry a much larger share of the current through the solution and occupy a larger share of sites at the cathode in the double layer. This should lead to a higher rate of manganic ion reduction and lower overall cell current efficiency.

One possible scheme to improve the cell current efficiency would be to carry out the electrolysis in a differential area electrode cell in which the cathode was smaller than the anode. The effect would be that at any anode current density, the cathodic current density would be higher. As seen before, this should result in relatively less manganic ion reduction at a given anodic current density. Several designs for differential area cells are possible. For example, one might simply mask part of one electrode. Another approach would be to construct a cell with concentric electrodes such as a rod in a tube. In our case, we took advantage

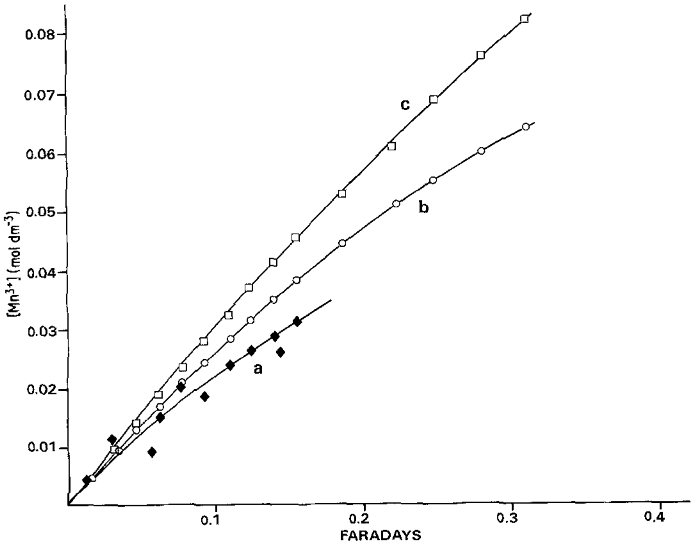

Fig. 8. Electrolyses at 66 mA cm^{-2} and (a) 90° C or (b) 70° C. Plot (c) was the result at 66 mA cm^{-2}, 90° C and a zirconium cathode.

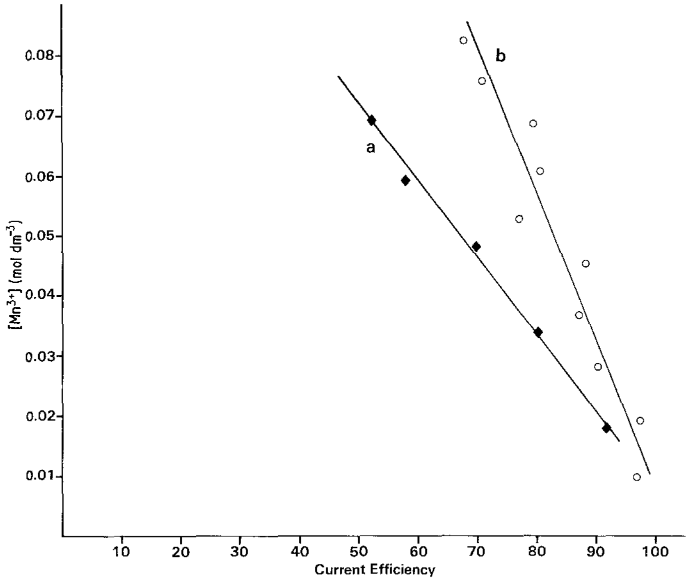

Fig. 9. Steady state current efficiencies against manganic ion concentration for (a) 132 mA cm^{-2}, 90° C graphite cathode and (b) 66 mA cm^{-2}, 90° C, zirconium cathode.

of the relatively large surface area of a 'smooth' graphite plate compared with the lower surface area of zirconium foil which we used as the cathode. The Zr foil was simply attached to the surface of the graphite plate which had been the cathode in all previous experiments. The results are shown in Fig. 8. Note that a major improvement in cell current efficiency is obtained. A plot of incremental current efficiency against manganic ion concentration is shown in Figure 9. Note that the experiment with the zirconium cathode gives a much higher current efficiency than the best run at the same temperature using parallel graphite electrodes.

The plot in Fig. 9 indicates the current efficiencies one would obtain in a steady state experiment in which manganic ion was removed or reacted (i.e., coupled to a chemical oxidation step) at the same rate as it was formed.

Although we have not optimized the generation of manganic ion in this system (a task that will most likely lead to differing conditions depending on the specific application), the effects of the major variables on cell current efficiency have been demonstrated. Most importantly it has been shown that very high cell efficiencies may be obtained in an undivided cell. This should result in considerable capital savings when compared to the cost of using a divided cell for a process in which manganic ion is desired.

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