

The Synthesis of Manganese(III) Acetate in Bipolar Packed-Bed and Trickle-Bed Electrode Cells

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In this research, the electrochemical oxidation of Mn(II) acetate to Mn(III) acetate was investigated in aqueous acetic acid solution, using a bipolar particulate electrode cell.

In order to determine the effect of flow modes on the yield of Mn(III) acetate, which is an important oxidizing agent and catalyst in organic reactions, a bipolar particulate electrode cell was employed both in flooded and trickle flow modes.

The experiments were conducted at controlled potentials of 50-250 volts using the solution (10% H₂O, 90% CH₃COOH, 0.1 M Mn(CH₃COO)₂.4H₂O, 0.1 M CH₃COONa.3H₂O) and at an optimum flow rate of 0.04 ml.s⁻¹.

The values of space-time yields for both electrode cells gave a maximum at about the same voltage range (4.5-5 V/number of layer). The maximum values obtained with approximately identical energy consumption values were 36.13 kg.m⁻³.h⁻¹ and 23.73 kg.m⁻³.h⁻¹ in a bipolar packed-bed and trickle-bed electrode cell, respectively.

Thus, the effectiveness of the flow modes using a bipolar particulate electrode cell has been demonstrated for the electrosynthesis of Mn(III) acetate.

Key words: Mn(III) acetate, electrosynthesis, packed-bed electrode cell, trickle-bed electrode cell

Introduction

In recent years, considerable work has been done on particulate electrode cells. These consist of individual electronically conducting particles with a system capable of operating in a bipolar or monopolar manner. For a bipolar bed to work, the electronically conducting particles must be isolated from each other. An alternative technique is to use a packed-bed of Raschig rings isolated from each other by means of a polyester net. When electric potential is applied across the bipolar electrode cell, every electrode particle is polarized and behaves as an anode on one side and a cathode on the other side¹. Thus, Faradaic reactions take place on both

sides of electrode particles. These electrode designs are characterized by very high specific surface areas and space time yields². One means of shortening the inter-electrode gap is to use a bipolar packed-bed cell, either in flooded or trickle mode³. Such cells can be constructed with gaps of the order of 1 mm, and are particularly appropriate because the high resistivity of electrolyte favours a low level of by-pass current. Furthermore, preliminary cyclic voltammetry studies have shown that only a small portion of the Mn(III) produced at the anodic surfaces is back reduced at the cathodic surface. These cells have been applied to water treatment^{4,5,6} and electroorganic synthesis processes^{7,8,9} where the liquid conductivity and the current density are not high. Electrolysis with bipolar particles can be performed in the modes of packed-bed, trickle-bed and fluidized-bed⁶.

The purpose of this present paper is to clarify the effect of flow modes such as flooded flow and trickle flow application to the graphite packed-bed electrode cell for the electrolytic production of Mn(III) acetate, which is an important oxidizing agent and catalyst in organic reactions,^{10,11,12} in aqueous acetic acid solution.

Experimental

Chemicals and analysis

The materials used were acetic acid (analytical grade), manganous acetate (BHD, described as $(\text{CH}_3\text{COOH})_2\text{Mn}\cdot 4\text{H}_2\text{O}$), and sodium acetate (Merck analytical grade, described as $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$). All were used as received. The electrolyte comprised a 0.1 M solution of manganous acetate in a 90% acetic acid/water mixture (by volume) with 0.1 M sodium acetate. Mn(III) was routinely determined either by UV visible absorption spectra or by titrating with measured excess of ferrous solution and back titration with standard dichromate solution, and results by both methods were in good agreement.

Experimental equipment

Figure 1 shows a schematic diagram of a bipolar packed-bed or trickle-bed electrode cell. The cell was made of two concentric glass tubes, the inner of which was 1.7 cm diameter, and 20 cm in total height. The temperature of the cell could be maintained at ambient temperature by cooling water passing the outer jacket. Graphite rods serving as feeder electrodes were fixed 18 cm apart vertically to the cell. Cylindrical graphite Raschig rings ($\phi=8\text{mm}$, $h=5.4\text{mm}$) were packed between two feeders. Polyester mesh, 1mm thick, was inserted between each layer, which consisted of three graphite Raschig rings, in parallel with the feeder electrodes, and the packed-bed was divided into 32 layers. Power from a 500/5A d.c. source was supplied to and withdrawn from the cell by feeder electrodes which made contact with the top and bottom layers, the top layer being rendered anodic. A perforated plastic plate (hole diameter=1mm, fractional free area=78%) was fixed 2 cm above the anode and used as liquid distributor in the case of trickle flow operation. Hewlett-Packard multimeters were used to monitor the applied voltage and cell current, respectively. The flowmeter used (Type LD 100, Nr 366, 611 Nra 51595) was calibrated at 16 °C for 0.1-2.0 $\text{lt}\cdot\text{h}^{-1}$ flow rates. The quantity of Mn(III) acetate electrosynthesized was recorded with a Jenway UV/Vis-6105 spectrophotometer.

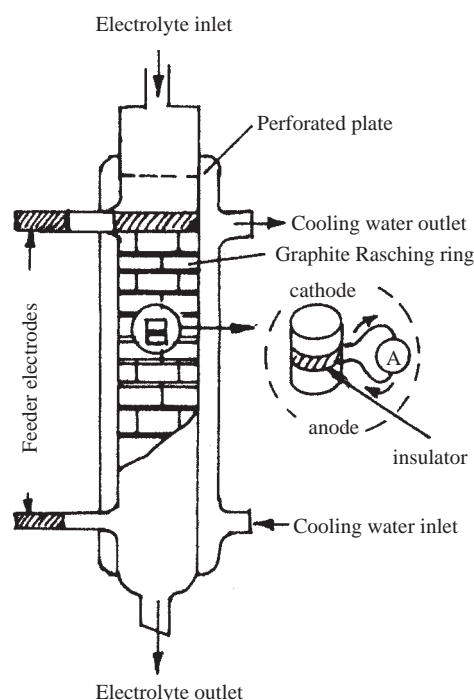


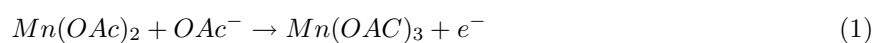
Figure 1. Schematic diagram of bipolar packed-bed or trickle-bed electrode cell.

Experimental Procedure

In the case of flooded flow mode, the electrolyte was given to the bed from the top, and it was operated while full of electrolyte. Then, the required flow rate was set and current was supplied to the cell. The experiments were conducted at flow rates of 0.04 ml. s^{-1} , which we determined as an optimum value in our preliminary studies. The product was collected and analyzed. Runs were carried out for a range of cell voltage (50-250 V). When the bed was operated in the trickle flow mode, the electrolyte was distributed to the top layer via perforated plastic plate at the same flow rate as we used in flooded flow, applying the same procedure.

Results and Discussion

Several preliminary experiments showed that the initial concentrations of manganous acetate, sodium acetate and water also affect the yield of product^{13,14}. Mn(II) acetate and sodium acetate concentrations were determined by their solubilities in acetic acid-water medium. During the experiments, the stability of Mn(III) ions was controlled by a higher concentration of Mn(II) acetate¹⁵. The space-time yield and solution conductivity were also taken into account in selecting the concentrations of these variables. For instance, sodium acetate concentration is likely to have two mutually opposing effects on the conversion ratio of manganese(II) acetate. The first is the obvious positive effect due to the nature of the reaction.



The second effect operates to reduce the conversion ratio, because the Kolbe reaction is facilitated by increased concentration of acetate¹⁶. For this reason, sodium acetate concentration was chosen to be the

same as the manganous acetate concentration (0.1M), considering our preliminary experiments¹⁷.

Furthermore, the water content of the solution is important for the degree of ionization of sodium acetate and hence for the conductivity of the solution. The ionization of the solvent (acetic acid) is also increased by higher water content. This helps to use lower cell voltages by increasing the concentration of hydronium ions to be reduced at the cathodes. Therefore, higher water contents bring about lower energy consumption. The only unfavorable effect of high water content is the deterioration of Mn(III) ions¹⁸. The use of tetrahydrate salt of manganese(II) acetate and trihydrate of sodium acetate limited the water content to 10% because of the instability of Mn(III) acetate in aqueous acetic acid solution.

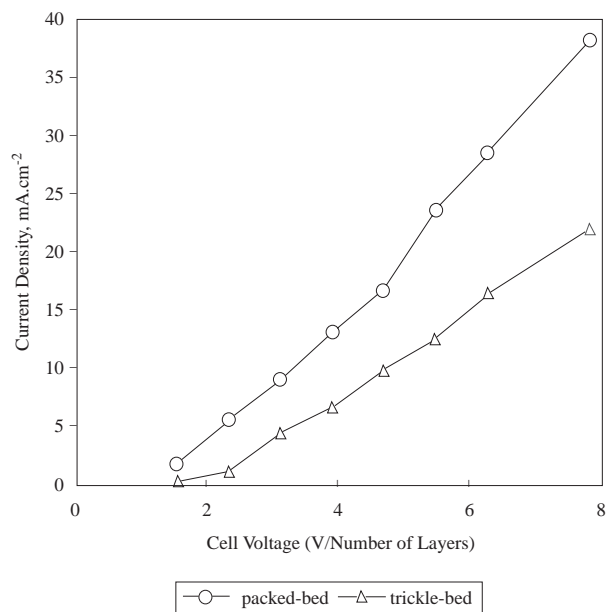


Figure 2. Variation of current density with cell voltage per number of layers in bipolar packed-bed and trickle-bed electrode cells.

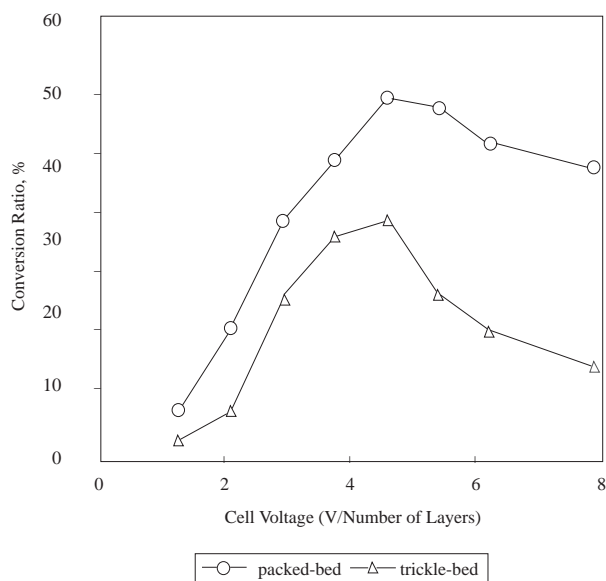


Figure 3. Variation of conversion ratio with cell voltage per number of layers in bipolar packed-bed and trickle-bed

electrode cells.

Since the conversion ratio of Mn(III) acetate decreases with increasing flow rates of solution, the optimum flow rate was chosen as 0.04 ml.s^{-1} due to electrolysis time on the electrode¹⁷.

Doubtless, the cell voltage is an obvious factor influencing the product yield in an electrolytic process. Therefore, the effects of cell voltage on the production yield of Mn(III) acetate were also investigated on both electrode cells. Figure 2 shows the current density versus the cell voltage (V/number of layer) curves. The Faradaic current in the trickle-bed electrode cell was lower than in the packed-bed electrode cell. This is accordance with the results of Kusakabe¹⁹.

Figure 3 indicates the variations of the conversion ratio of Mn(II) acetate to Mn(III) acetate with cell voltage (V/number of layer). The maximum conversion ratio of Mn(II) acetate were obtained in the 4.5-5 cell voltage (V/number of layer) range in both packed-bed and trickle-bed. The maximum conversion ratio of Mn(II) acetate in the bipolar packed-bed electrode cell reached 49.6%, whereas this value was obtained as 32.6% in the trickle-bed electrode cell.

Since the conversion ratio of the Mn(II) acetate is not the only criterion for the efficiency of electrochemical reaction, the results were interpreted in terms of cost-sensitive parameters such as current efficiency, energy consumption and space-time yield.

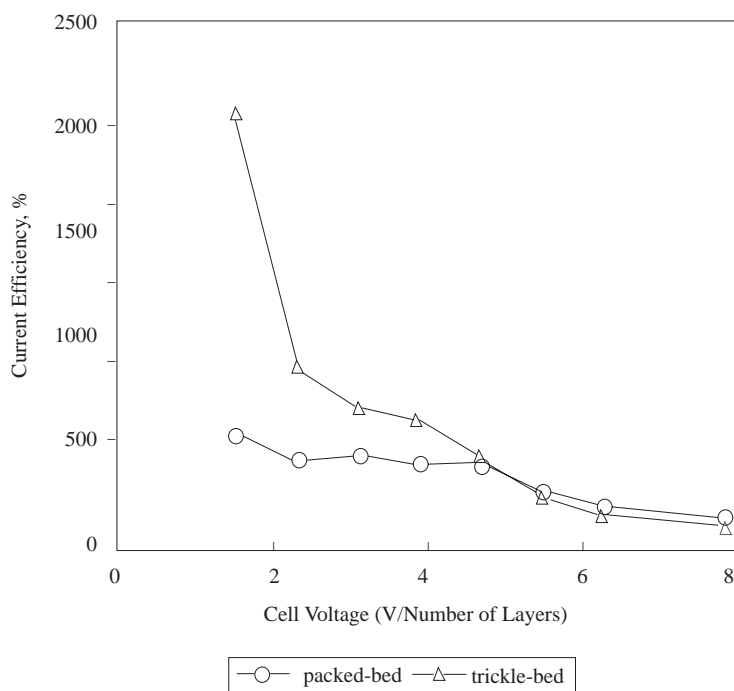


Figure 4. Variation of current efficiency with cell voltage per number of layer in bipolar packed-bed and trickle-bed electrode cells.

From this point of view, the relationship between the cell voltage (V/number of layer) and current efficiency are given in Figure 4. It can be seen that the current efficiency values exceeded the 100% level. This is the result of the occurrence of competing catalytic reactions besides the electrochemical reaction and the behavior of Mn(III) species in aqueous acetic-acid media. It can also be seen from Figure 4 that the current efficiency in the trickle-bed is higher than in the packed-bed cell, especially at lower cell voltage (V/number of layer). The current efficiency that we observed decreased and the energy consumption increased with hydrogen evolution at higher voltages, as shown in Figures 4 and 5. The sharp increase

of energy consumption in the trickle-bed electrode cell is due to higher bypass current density. The bypass current density was dependent on the electrical conductivity of the electrolyte and the bed configuration⁶.

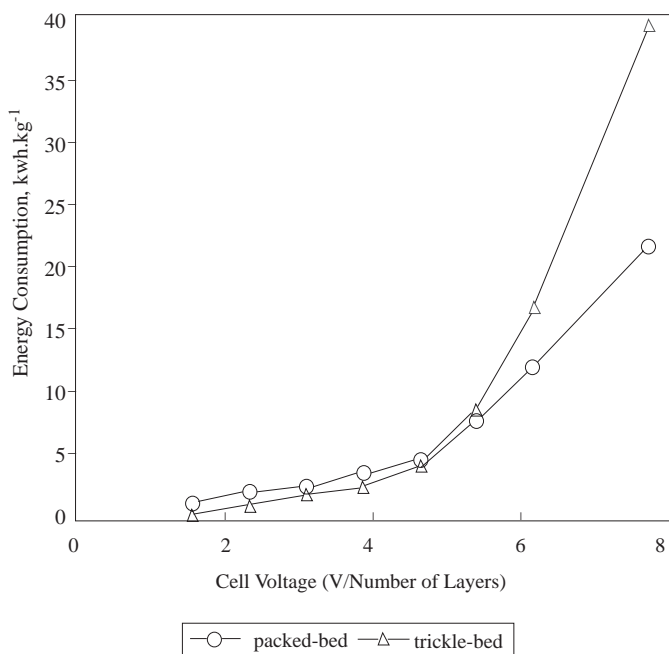


Figure 5. Variation of energy consumption with cell voltage per number of layer in bipolar packed-bed and trickle-bed electrode cells.

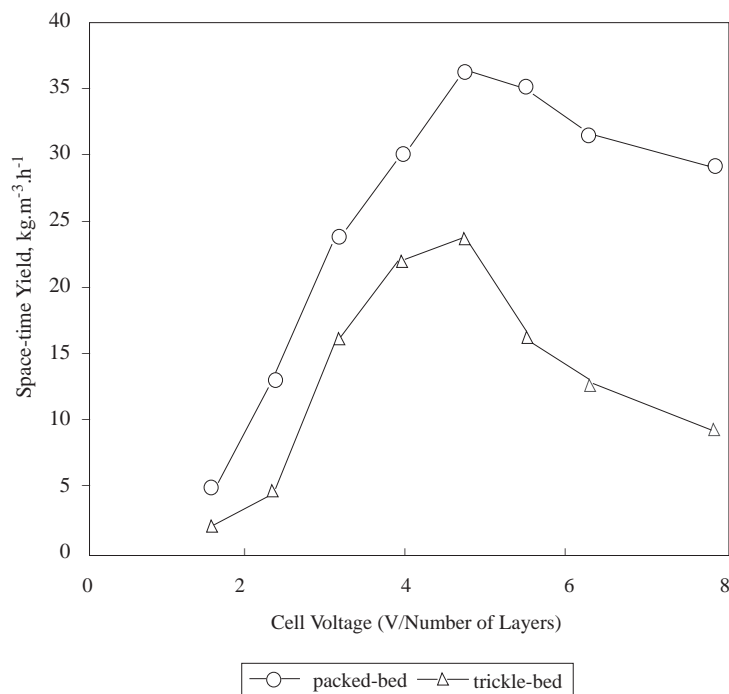


Figure 6. Variation of space-time yield with cell voltage per number of layer in bipolar packed-bed and trickle-bed electrode cells.

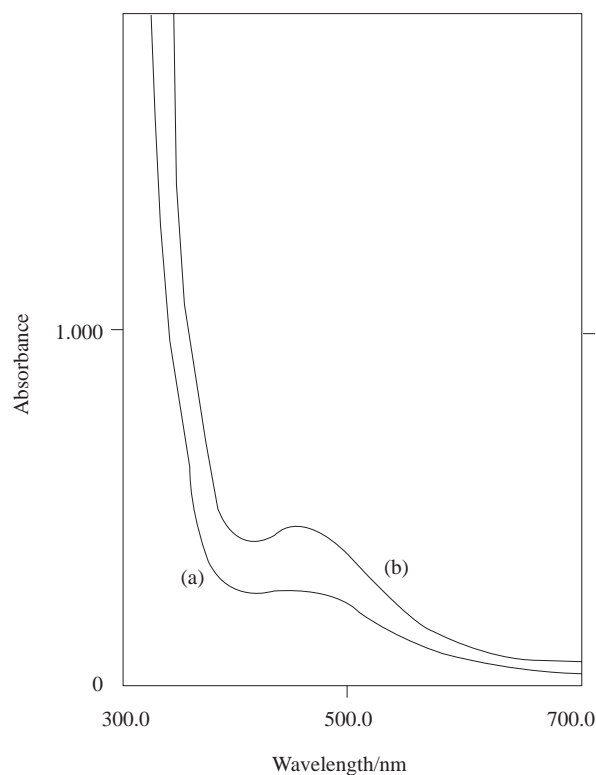


Figure 7. UV visible spectra of (a) standard Mn(III) acetate, (b) Mn(III) acetate obtained

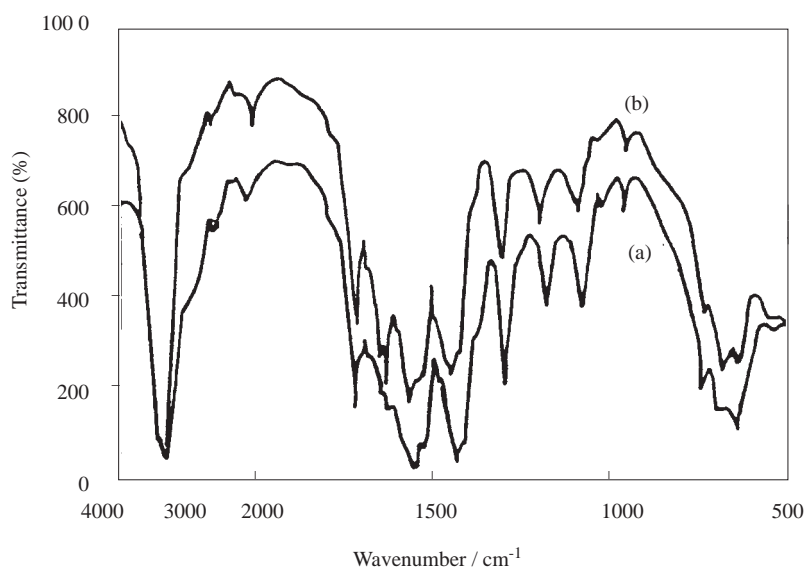


Figure 8. Infrared spectra of (a) standard Mn(III) acetate, (b) Mn(III) acetate obtained

From Figure 6 it is seen that the values of space-time yields for both electrode cells gave a maximum at about the 4.5-5 cell-voltage (V/number of layer) range. The maximum values achieved with approximately identical energy consumption values were $36.13 \text{ kg.m}^{-3}.\text{h}^{-1}$ and $22.15 \text{ kg.m}^{-3}.\text{h}^{-1}$ in bipolar packed-bed and trickle-bed electrode cells respectively.

Moreover, the spectrum of the manganese(III) acetate obtained was compared with those of UV and IR of the standard, and excellent agreement was found between them, as shown in Figures 7 and 8.

Conclusion

- Bipolar graphite packed-bed electrode cell operated in the flooded mode represented a significant improvement in performance in comparison with the trickle-flow mode.
- In the case of flooded-flow mode, the conversion ratio of Mn(II) acetate and space-time yield were increased approximately 50%.
- In the present study, the effectiveness of flooded-flow mode has been demonstrated for the electrosynthesis of Mn(III) acetate according to the experimental conditions.

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