Study of the Effect of Number of Layers on the Electrosynthesis of Cobalt(III) Acetate in a Bipolar Packed-Bed Flow Reactor

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Cobalt(III) acetate, which is an important oxidizing agent and catalyst in organic reactions, was electrosynthesized from cobalt(II) acetate solution in a bipolar packed-bed flow reactor.

In order to determine the effect of the number of layers on the yield of cobalt(III) acetate, experiments were performed in three different lengths of bipolar electrode cells, namely 16, 29 and 55 layers of graphite Raschig rings.

The experiments were carried out at controlled potentials of 50-450 V, measuring the total current and using the solution (5% H_2O, 95% CH_3COOH, $0.06MCo(CH_3COO)_2.4H_2O$, 0.2M $CH_3COONa.3H_2O$) at 298 K and 0.133 $L.h^{-1}$ flow rate.

According to the experimental results, the production of cobalt(III) acetate with the conversion ratio of 43% and the space-time yield of 35.9 $kg.m^{-3}.h^{-1}$ showed that 29 layers was the optimum.

Key Words: Electrosynthesis, Cobalt(III) acetate, Packed-bed flow reactor, Bed length

Introduction

The development of electrochemical reactor systems with high surface areas has been one of the most active research field in industrial electrochemistry. The particulate electrode cell, including packed-bed and fluidized-bed types, is one of these systems and it has attracted much attention recently. These cells consist of individual particles having electrical conductivity[1]. Fluidized-bed cells provide a high surface area, but their main limitation is that the fluidization of the bed causes a loss of electrical contact between the particles, resulting in an extensive ohmic drop within the cell. In this case, uniform potential and current distribution cannot be maintained. Many of the problems of fluidized-bed cells appear to have been overcome by the development of the three-dimensional contiguous-bed reactor. These reactors are characterized by very high specific surface areas and space-time yields, and can be operated as bipolar or monopolar systems. In particular, the packed-bed design is far superior to the fluidized one due to the ability of control potential and current distribution through the electrode bed[2].

A large number of interrelated factors should be considered during the selection of a particular reactor design and the development of new ones. The design of cells with minimum resistance is a major problem

in an electrochemical process. Clearly, the internal cell resistance, R_{Cell}, is decreased by making the inter-electrode gap smaller. One way of shortening the inter-electrode gap is to use a bipolar packed-bed cell either in flooded or trickle mode[3].

Kusakabe et al.[4−6] carried out the reduction of Cu(II) ions in a bipolar packed-bed electrode cell and determined the effects of particle diameter, cell voltage, packing mode and electrolyte compositions on the overall current efficiency. Their results indicated that overall current efficiency rises with increasing Faradaic current (current passing through particles) compared to total current and also with the decreasing conductivity of the electrolyte.

Öğütveren et al.[7] investigated the behavior of a bipolar trickle bed of graphite Raschig rings for the production of Co(III) acetate, and the space-time yield obtained was 18 kg.m^{-3}.h^{-1}.

Furthermore, Goodridge et al. investigated the behavior of bipolar packed-bed electrodes using a rod cell operated in the flooded mode for the production of hypbromite and the epoxidation of styrene. They interpreted their results in terms of two cost-sensitive parameters, such as energy consumption and space-time yield, and they declared that this electrode system had exhibited attractive qualities for industrial electrosynthesis, particularly due to its low energy consumption and high space-time yields[1].

In our previous study, the effect of flow modes for both flooded and trickle flow, using a bipolar packed-bed electrode cell, was investigated for the electrosynthesis of manganese(III) acetate. Our results indicated that the flooded mode represents a significant improvement in performance compared to the trickle one[8].

The number of layers in a bipolar packed-bed flow reactor is an important parameter before doing the scale-up. Up to now, the effect of the number of layers (bed length) of the three-dimensional electrode cell has not been clarified[3]. The purpose of this research is to investigate the effect of the number of layers on the production of cobalt(III) acetate, which is the most commonly used autoxidation catalyst in the industrial oxidation of hydrocarbons[9−11], using bipolar packed-bed flow reactors designed with three different numbers of layers operated in flooded mode.

Experimental

Materials and Analysis

The materials used were glacial acetic acid (Merck, analytical grade), cobaltous acetate (BHD, described as $(CH_3COO)_2Co.4H_2O$), and sodium acetate (Merck, analytical grade, described as $CH_3COONa.3H_2O$). All were used as received. The electrolyte comprised of a 0.2 M solution of sodium acetate in a 95% acetic acid/water mixture (by volume), with 0.064 M Co(II) acetate. The concentration of Co(III) acetate was routinely determined by titration with aqueous sodium thiosulfate using starch as indicator, but the results were checked from time to time by UV visible spectrophotometry at 610 nm, a wavelength where only cobalt(III) is absorbed.

Electrode cells and associated equipment

The experiments were carried out using the bipolar electrode cells with three different numbers of layers (16, 29 and 55 layers) equipped with graphite Raschig rings, in a flooded flow mode. The electrode cells, which were made of two concentric glass tubes, were 1.7 cm in constant diameter and 14, 22, 40 cm in total height

for 16, 29 and 55 layers of Raschig rings, respectively. Three graphite Raschig rings (ϕ=8mm, h=5.4mm) were placed vertically in each layer. Electrochemical insulation between each layer was made by using 8 mesh polyester net (1 mm thick). The temperature of the column was kept at 298 K by cooling with water passing through the outer jacket. Power from a 500V/5A DC source was supplied to and withdrawn from cells by graphite rods serving as a feeder electrode, which made contact with the top and bottom layers of graphite Raschig rings. These feeders were located vertical to the electrode cells and the distance between them was 10, 18 and 35 cm for 16, 29 and 55 layers of graphite Raschig rings, respectively. The opposite face of each electrode has different polarities according to the voltage field caused by the bipolar connection (Figure 1). Hewlett-Packard multimeters were used to monitor the applied voltage and cell current. The flowmeter used (Type LD100, Nr366, 611 Nra91595) was calibrated at 16°C for 0.1-2.0 L.h^{-1} flow rates. The quantity of the Co(III) acetate electrosynthesized was measured with a Jenway U.V./Vis.-6105 spectrophotometer.
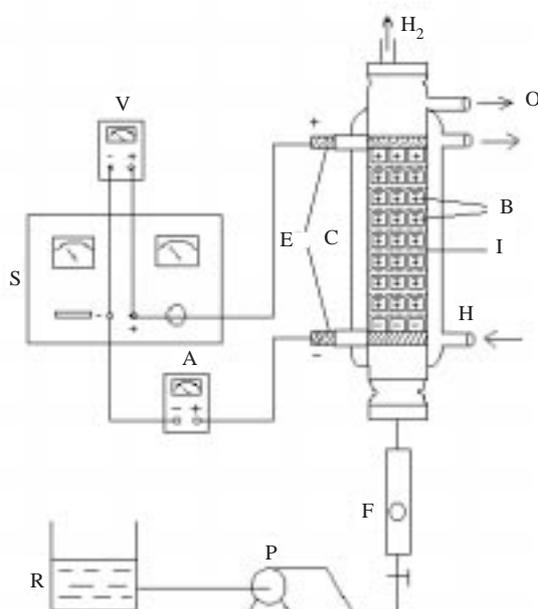

Figure 1. Schematic of the flow circuit and associated equipment for the continuous process: C-cell; E-feeder electrodes; H-cooler jacket; F-flowmeter; P-peristaltic pump; R-reservoir; O-product outlet; V-voltmeter; A-ampermeter; S-power supply; B-bipolar graphite Raschig ring layers; I-insulator.

Experimental procedure

Electrolyte was fed into the reactor from the bottom of the bed. The reactor was operated as a liquid full bed. The feed flow rate was adjusted to 0.133 L.h^{-1}. The experiments were carried out in a range of cell voltage from 50 to 450 V. The total current was measured for each cell voltage and it was kept constant in a range of 7-200 mA. The product was collected and analyzed. The same procedure was applied to each electrode cell.

Results and Discussion

The design of a cell with minimum internal cell resistance can be provided by using a highly conductive electrolyte such as acetic acid in water. On the other hand, the concentration of the electro-active species is

the major parameter that determines both the maximum feasible current density and the optimum space-time yield[3]. Several preliminary experiments showed that the initial concentrations of cobalt(II) acetate, sodium acetate and water content also affect the conversion ratio which is defined as

$$\theta = [Co(III)]/[Co(II)]_0 \tag{1}$$

where $[Co(II)]_0$ is the Co(II) concentration at the beginning of the electrolysis.

The composition of the electrolyte was selected on practical and logical considerations. Co(II) acetate concentration was limited by its solubility in acetic acid. Sodium acetate was added to support the electrolyte and its concentration was chosen to be higher than that of Co(II) with regards to the two mutually opposing effects on the conversion of Co(II) acetate[12]. The water content of the solution is important for the degree of ionization of sodium acetate and hence for the conductivity of the solution. Furthermore, the ionization of the solvent (acetic acid) is also increased through higher water content[8]. Thus higher water content favors lower energy consumption, but the only unfavorable effect of high water content seems to be the increased hydrolysis rate of the product[12,13]. For an undivided cell, Trivedi and Dhawan obtained higher Co(III) acetate yields by lowering the water content of the electrolyte[9]. In this study, the tetrahydrate salt of cobalt(II) acetate and trihydrate of sodium acetate were used and in the manner explained above the water content of the solution was limited to 5% .

The feed flow rate was chosen as 0.133 L.h^{-1} according to the preliminary experiments[14]. The conversion ratio of Co(II) acetate decreased as a result of the increasing flow rate of the solution. This was an expected result due to the decreasing retention time of the Co^{2+} ions at the anode. It also decreased with a reduced flow rate of solution because the cyclic voltammetry studies showed that if an undivided cell is used, only a small portion of Co(III) produced at the anodic surface is back reduced at the cathodic surface[7].

It is essential always to consider several figures of merit (such as the cell voltage, the conversion ratio of reactant to product, the current efficiency, the energy consumption and the space-time yield). Such comparisons should be made under similar process conditions. The cell voltage, or current density is, in many cases, a major factor controlling the current efficiency, the space-time yield and the product quality[3]. In presenting results, the total current measured was converted to a current density, j, calculated by dividing the total current to the area of three Raschig rings. Figure 2 shows that the current densities observed vary according to the cell voltage applied per number of layers for each electrode cells. For a given cell voltage, lower current densities were obtained with lower numbers of bipolar layers.

The conversion ratios of Co(II) acetate versus cell voltage per number of layers are depicted in Figure 3. The conversion ratio of Co(II) acetate in the packed-bed reactor of 16 layers increased from 16.8 to 27.3% while the cell voltage per number of layers variyied from 3.1 to 12.5 V. After increasing the voltage per number of layers to 20.3 V the ratio went down to 10.9%.
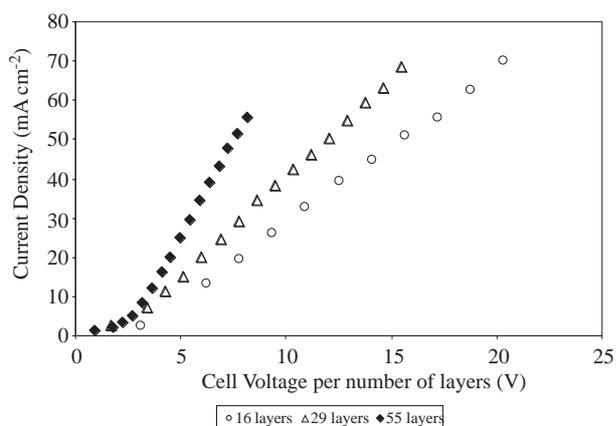
Figure 2. Variation of current density with cell voltage per number of layers in the bipolar packed-bed electrode cells with 16, 29 and 55 layers.
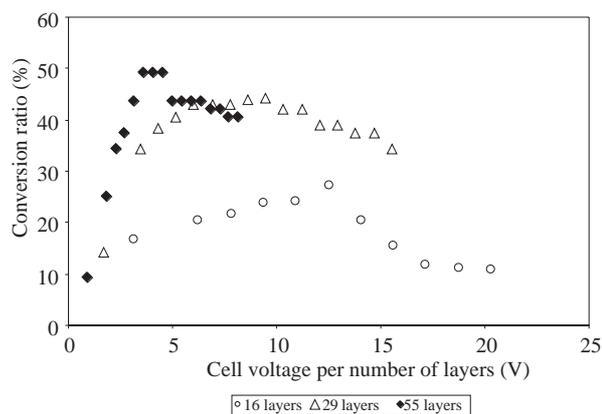
Figure 3. Variation of conversion ratio with cell voltage per number of layers in the bipolar packed-bed electrode cells with 16, 29 and 55 layers.

In order to compare the effect of the number of layers on the conversion ratio of Co(II) acetate, a second group of experiments were performed in a reactor having 29 layers. Increasing the voltage per number of layers from 1.7 to 9.5 V increased the conversion ratio from 14.2 to 44.1% (Figure 3), whereas increasing the voltage per number of layers 15.5 V had a significant decreasing effect on the conversion ratio (34.4%).

The experiments were carried out in bipolar reactor of 55 layers to investigate the effect of further increasing the number of layers in the reactor. The maximum Co(III) yield of 49.2% was obtained at cell voltage per number of layers of 4.5 V and current density of 19.7 mA.cm^{-2} (Figure 3).

The lowest conversion ratio was obtained in a packed-bed with 16 layers, as expected. In that, when electric potential is applied across the bipolar particulate the electrode cell, every electrode is polarized and behaves as an anode on one side and as a cathode on the other side. Thus, Faradaic reactions take place on both sides of the electrode particles[5].

Therefore regenerative oxidation occurs at the anode according to the reaction

$$Co^{2+} \rightarrow Co^{3+} + e^- \quad E^0 = -1,82V \tag{2}$$
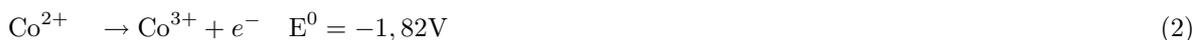
In an acetic medium containing 5-10% of water, oxygen evolution should be taken into consideration. As a result, the competing reaction oxygen is evolved[7].

$$2OH^- \rightarrow 1/2O_2 + H_2O + 2e^- \quad E^0 = -0,401V \tag{3}$$

If an undivided cell is used the reaction occurring at the cathode is

$$Co^{3+} + e^- \rightarrow Co^{2+} \quad E^0 = 1,82V \tag{4}$$

$$2H^+ + 2e^- \rightarrow H_2(g) \quad E^0 = 0,00V \tag{5}$$

Increasing the number of layers in the electrode cell resulted in an increase in the conversion ratio. As shown in Figure 3, the conversion ratio of Co(II) acetate increased significantly ∼61% when increasing the number of layers from 16 to 29. However further increasing the number of layers to 55, it rose only 10%. It

was clarified that further increasing the number of layers caused an undesirable secondary electrochemical reaction.

In industrial electrochemical processes one should obviously pay great attention to economic considerations. From this point of view, to determine the effect of number of layers on the yield of Co(III) acetate, other efficiency parameters such as current efficiency, C_e, energy consumption, E_c, and space-time yield, ρ_{st}, need also be considered. In the present study, these efficiency parameters were calculated by the following equations from the experimental result obtained under the same process conditions as described in the experimental section.

$$C_e = 100 \ \Delta c \ n \ F/ \ I_t t \tag{6}$$

$$E_c = \ n \ F \ E \ / \ M \ C_e \tag{7}$$

$$\rho_{st} = \Delta c \ M/ \ V_e t \tag{8}$$

where Δc is the amount of produced cobalt(III) acetate (mol), I_t the total cell current (A), F the Faraday constant $(As.mol^{-1}.e^{-1})$, E the applied cell voltage(V), M the molar mass of the cobalt(III) acetate $(kg.mol^{-1})$, t the electrolysis period(s), n the number of electrons involved in electrode reaction (dimensionless) and V_e the total electrode volume (m^3).

Figure 4 shows how the current efficiency observed varies with the cell voltage per number of layers for the electrode cells. Lower current efficiency values were obtained with the increasing cell voltages per number of layers in all cases. Current efficiency observed above 100% at lower voltages appears as a result of competing catalytic reactions, such as oxygen evolution beside the electrochemical reaction. It may be declared that, in the presence of oxygen, cobalt(III) acetate is generated not only by anodic electrooxidation of the cobalt(II) acetate, but also by using molecular oxygen by the following reaction[15]:

$$2Co(OAc)_2 + \ 3HOAc + O_2 \rightarrow 2Co(OAc)_3 + \ CH_3OH \ + \ H_2O + \ CO_2 \tag{9}$$
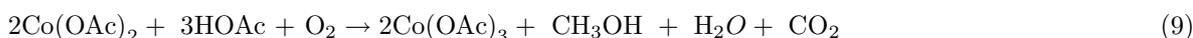
Furthermore, the electrochemical reaction takes place on each graphite Raschig ring surface as well as on the plate electrodes. Therefore, the bipolar packed-bed electrodes behave as if many plate electrodes were arranged in series. Similar results can be seen in the literature[4,7].

From Figure 5, it is seen that values of energy consumption increased with the rise in cell voltage where the values of current efficiency decrease as shown in Figure 4. The variation of space-time yield with the cell voltage per number of layers is shown in Figure 6. It can be seen from this figure that the lowest space-time yield was obtained with the use of the cell with 55 layers. This clarified the fact that an electrode volume of 55 bipolar layers is much higher than that of 29 bipolar layers, which obtained nearly the same conversion ratio of cobalt(II) acetate.
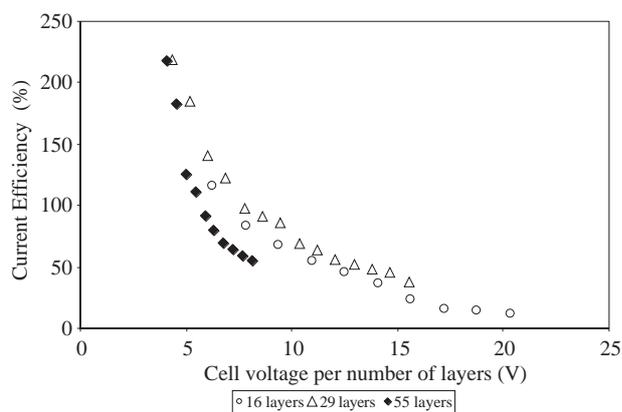
Figure 4. Variation of current efficiency with cell voltage per number of layers in the bipolar packed-bed electrode cells with 16, 29 and 55 layers.
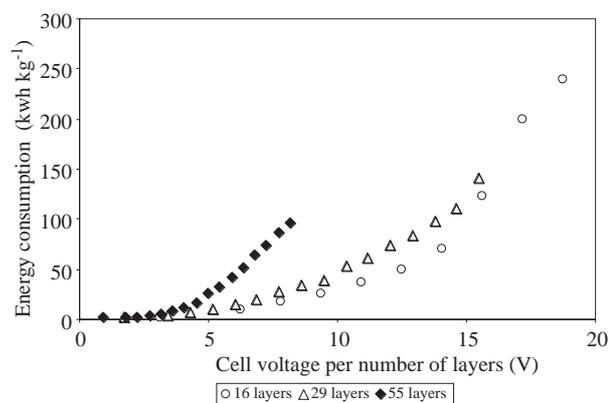
Figure 5. Variation of energy consumption with cell voltage per number of layers in the bipolar packed-bed electrode cells with 16, 29 and 55 layers.
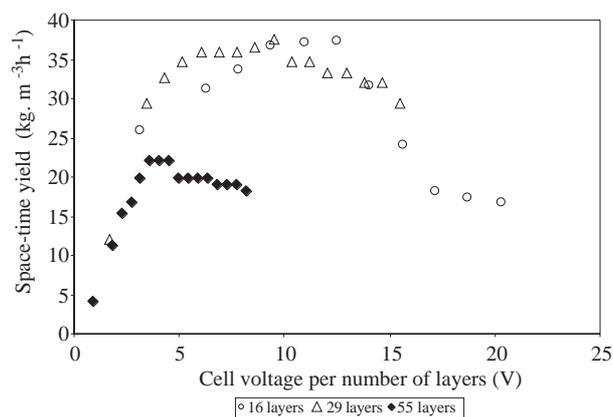

Figure 6. Variation of space-time yield with cell voltage per number of layers in the bipolar packed-bed electrode cells with 16, 29 and 55 layers.

Conclusion

The aim of this work is to investigate the effect of the number of layers using bipolar packed-bed reactors on the conversion ratio of cobalt(II) acetate regarding cost-sensitive parameters such as current efficiency, space-time yield and energy consumption. According to the experimental results, the main conclusions are as follows:

- The increase in the number of layers from 16 to 29 increased the conversion ratio of Co^{2+} ions, but a further increase in the number of layers (to 55) had no significant effect and also led to a major decrease in space-time yield and resulted in an increase in energy consumption.

- Bipolar reactors with 16 and 29 layers displayed nearly the same current efficiency, space-time yield and energy consumption values.

- When the bipolar packed-bed electrochemical reactor with 16 layers was compared to that of 29 layers the second was found to be the one having the optimum number of layers in terms of a higher conversion ratio of cobalt(II) acetate.

- As a result, cobalt(III) acetate was produced using the cell with 29 layers with the optimum conversion ratio of 43%, current efficiency of 98.1%, energy consumption of 26.5 kwh.kg^{-1} and space-time yield of 35.9 kg.m^{-3}h^{-1} at 7.8 V/ layer.

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