Multi-cathode cell with flow-through electrodes for the production of iron(ii)-triethanolamine complexes

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Nonregenerable reducing agents used in dye houses for the application of indigo, vat dyes and sulfur dyes can be substituted by indirect cathodic reduction techniques. An electrochemical cell for the indirect cathodic reduction of dispersed indigo dyestuff using an alkaline solution of the Fe(iii/ii)-triethanolamine complex as redox mediator was constructed and tested. The cell is built up as divided cell (cathode area 5–10 m^2, catholyte volume 12 L, anolyte volume 1.5 L) with several three dimensional cathode units (up to 10) in the same cathode compartment. The cathodes were connected to a common anode and to separately adjustable power supplies. The catholyte was circulated through the porous cathode units parallel to the current direction. Two different electrode materials (copper and stainless steel) and cathode constructions were tested, resulting in an optimized cell construction. The electrochemical cell was characterized by a series of batch electrolysis experiments. Results are given dealing with the cell voltage drop in the cathode, the product yield and the current efficiency at different current densities and cell current. After an optimization step the current efficiency reaches 70–80% at 2 A m^{-2} current density and 7.8×10^{-3} mol dm^{-3} Fe(ii)-complex. The cell current is 10 A.

1. Introduction

The indirect electrochemical reduction of dispersed textile dyestuff (e.g. indigo, vat dyes, sulfur dyes) into the alkaline soluble leuco-form can be mediated by a Fe(ii/iii)-triethanolamine (TEA) complex [1–4]. This substitution of non-regenerable reducing agents (e.g. dithionite, formaldehyde-sulfoxylates, sulfinic acids, hydroxyacetone, glucose) for the reduction of vat dyes, indigo, and sulfur dyes by electrochemical methods offers economic and ecological advantages for the textile dye houses. As described in previous publications the cathodic reduction is running with low current density, for example, 4–5 A m^{-2} (catholyte: 2.4×10^{-2} mol dm^{-3} Fe^{3+}, 0.23 mol dm^{-3} TEA, 0.5 mol dm^{-3} NaOH) [1, 5]. An increase of the concentrations of the electrochemically active iron–TEA complex is limited due to the costs resulting from the chemical-input in the dye house and further pollution of the waste water in the case that no mediator recycling is planned [6]. For a successful application of this new reduction process in dye houses the development of a suitable electrochemical reactor with sufficient power is necessary. The anodic reaction is liberation of oxygen which allows much higher current densities thus being of minor importance for the cell development at this time. Therefore, an asymmetrical cell with maximum cathode area had to be developed to realize the large cathode area required for the reduction process at minimized anode area and cell volume.

Many different electrode arrangements are described in the literature to enlarge the electrode surface of the electrochemical cell under given conditions, for example, the use of fluidized bed or fixed bed flow-through electrodes, the use of special cell constructions as the Swiss roll cell or the capillary gap cell [7–14]. Another principle of cell construction uses several cathodes or anodes in the same electrolyte where potential differences caused by the varying distance of the electrodes to the counter electrode(s) are compensated by individual current sources for each electrode [15].

The construction described in this article is a divided cell basing on a combination of a fixed bed flow-through electrolyser with cell containing multiple cathodes and a common anode [5, 15]. In the combination of a multicathode cell and porous flow through electrodes the advantages of both principles are combined and a high specific electrode area can be realized.

Experimentally determined results of the cell voltage drop within the cathode, the product yield and the current efficiency at different cell current/current density and catholyte concentrations are given.

Efforts were made to optimize the construction in view of a technical realization of the reduction process.

2. Experimental details

2.1. *Construction of the electrochemical cell*

The cell was constructed as divided cell because the cathodic reduction process affords a strict separation

of the catholyte from the anodic side. The reactor vessel containing about 12 L of catholyte and 1.5 L of anolyte was manufactured from polyethylene.

Two different separator materials were used (sintered glass porosity D4, Schott; cation exchanger membrane, Thomapor MC-3470).

The tested electrodes were manufactured from copper wire (copper wire, dia. 0.1 mm) or woven stainless steel fabric (steel 1.4404, aperture size 0.315 mm, wire diameter 0.2 mm, open area 37%, Haver and Boecker, Oelde, Germany). The front area of the electrodes was 400 cm^2 (20 cm × 20 cm).

For manufacturing of the copper wire electrodes 15 ropes, each with a wire length of 260 m, were mounted on a rectangular frame (20 cm width × 25 cm height) to give a porous flat cathode unit (area 1.25 m^2). The volume of the catholyte in the cell was adjusted at 80% of the height of the electrode thus giving an electrode area of 1 m^2 per cathode unit. As shown in Fig. 1 up to 10 cathodes were mounted in the cell and a total cathode area of 10 m^2 could be reached with a cathode front area of 400 cm^2. The distance between two cathode units was 20 mm to avoid short circuits.

In the experiments with the copper electrodes a separator manufactured from sintered glass was installed.

The stainless steel cathodes were manufactured by folding a piece of woven steel fabric to give a cathode consisting of six layers of cloth (ca. 20 cm × 20 cm). One of the layers of such a cathode unit serves as connection for the current supply. A single cathode unit has an electrode area of 0.5 m^2 (10 cathode units 5 m^2) while the front area remains 400 cm^2. The plane steel cathode units were mounted in the cell to form a sandwich like cathode consisting of up to 10 cathode units separated by insulating layers of polyethylene

fabric. Thus the space between the cathode units could be reduced to 2–3 mm.

In the experiments with the stainless steel electrodes a cation exchanger membrane (Thomapor MC-3470) was used as separator.

As iron was frequently deposited on the cathode units [5] and to obtain a defined surface of the electrode material a cleaning operation with diluted salpetric acid (copper cathodes) or diluted sulfuric acid (stainless steel cathodes) followed by extensive rinsing with water was performed before the electrolysis experiments.

The catholyte was circulated through the cathodes parallel to the current direction (Iwaki magnetic coupled centrifugal pump MD 30R) with a flow of 14–15 L min^{-1} (copper wire cathodes) and 17.5 L min^{-1} (woven stainless steel fabric). The catholyte flow was about 0.6 cm s^{-1} in the cathode compartment and assuming a porosity of 50% in the cathode a catholyte flow through the porous cathodes of up to 1.2 cm s^{-1} was reached.

A stainless steel wire cloth served as anode in a solution of caustic soda. Due to insufficient chemical stability the stainless steel anode was replaced during the course of the experiments by a platinum coated titan electrode (Heraeus Elektrochemie, Rodenbach, Germany).

No additional agitation was needed in the anolyte because the anodic liberation of oxygen caused sufficient turbulence.

The experiments were performed at room temperature.

A commercial electric power supply (Delta Elektronika SM 30-100, The Netherlands) unit was used as main current source for the cell. The current was divided equally to the cathode units by adjustable resistors constructed with power transistors.

For the voltammograms of single cathode units the potential of the cathodes was measured at the front side of the cathode unit by a laboratory potentiometer (Metrohm 654 pH-meter, Herisau, Switzerland). All potentials are given with respect to a Ag /AgCl, 3 M KCl reference electrode.

2.2. *Chemicals and analytical procedures*

The catholyte was prepared according to the procedure described in a previous publication [1]. The Fe$_2$(SO$_4$)$_3$, the triethanolamine (TEA), the NaOH and the Indigo Plv. (BASF) were of technical grade. In the tests using the ceramic separator a solution of the mediator (catholyte) was used as anolyte to avoid disturbing effects due to a slight bleeding of the separator. In the tests using a membrane separator 1 mol dm^{-3} NaOH was used as anolyte.

Two different methods were used to determine the amount of reduced Fe(II)-TEA complex in the catholyte. In the tests of the copper electrodes the catholyte was analysed by potentiometric titration with 0.1 mol dm^{-3} K$_3$[Fe(CN)$_6$] as titrand [16]. This method allows the advantageous direct titration of
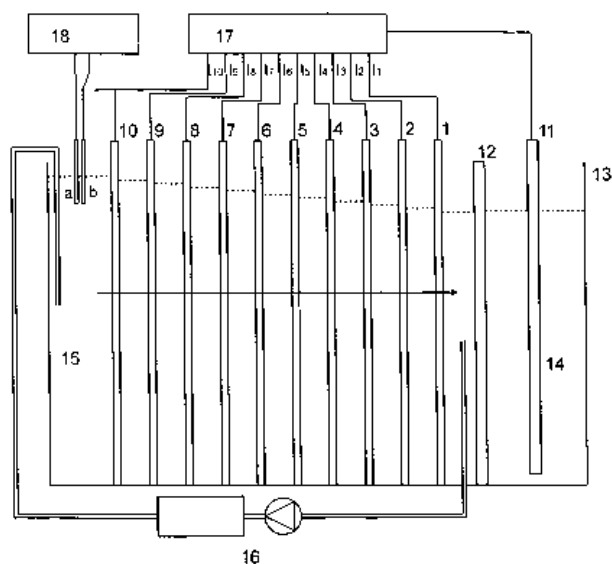

Fig. 1. Scheme of the electrolytic cell containing 10 cathode units (1–10) and one common counter anode (11), separator (12), vessel (13), anolyte (14), catholyte (15), catholyte circulation pump and flow meter (16), adjustable current supply I_1–I_{10} (17), potentiometer (18) with reference electrode (a) and Pt-electrode (b).

the catholyte without further addition of chemicals which is a favourable method when reduced dyestuff for example, indigo is present in the catholyte. The considerable sensitivity of the analysed sample against oxidation by air oxygen causes somewhat lowered values in the results and reduces the calculated current efficiency and turnover.

In the determination of the current efficiency by potentiometric titration of the catholyte with $0.1 \, \text{mol dm}^{-3}$ $KMnO_4$ as titrand the catholyte sample was acidified with sulfuric acid. These solutions of Fe(II) are not sensitive against air oxidation but can be analysed only in absence of reducible indigo dyestuff. In the titration against $KMnO_4$ a correction must be determined by internal standardization for the mediator system concerned in order to allow for oxidative side reactions during the titration.

3. Results and discussion

3.1. *Characterization of the cathode units*

For the Fe(III/II)-TEA complex used as catholyte the limiting current density is fixed by the current plateau of the diffusion controlled cathodic reduction according to Equation 1 [1].

$$Fe(III)TEA + 1e^{-} \rightarrow Fe(II)TEA \qquad (1)$$
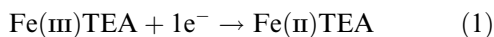
When the current density exceeds this limit the liberation of hydrogen and the deposition of elemental iron lower the current efficiency of the electrode reaction. The current plateau for a fixed mediator concentration at a given electrolyte flow is easily determined when plane electrodes are used [5].

In the case of three-dimensional flow-through electrodes no significant diffusion limited current plateau can be determined.

Investigations on plane electrodes proved that the presence of indigo dyestuff causes no disturbing effects on the electrode reaction [1, 5]. To avoid complications due to the coupled reduction of indigo dyestuff, deposited pigment or reoxidized dyestuff most of the tests described below were performed in absence of the dyestuff.

For a first characterization the voltammograms of single electrode units mounted in different positions of the cell were recorded to prove the similarity of the different electrode positions. Figure 2 shows the voltammograms recorded using a single three dimensional copper electrode with an electrolyte flow through the cathode units of 14–$15 \, \text{L min}^{-1}$. The used catholyte contained $2.4 \times 10^{-2} \, \text{mol dm}^{-3}$ Fe^{3+}, $0.23 \, \text{mol dm}^{-3}$ TEA and $0.5 \, \text{mol dm}^{-3}$ NaOH. The experiments were performed at room temperature.

The cathode position 1 is nearest to the separator and gives a slightly changed voltammogram due to geometric inaccuracies, which become more important at short distance to the anode and higher current.

The equivalence of the different cathode positions can also be seen in Fig. 3 where the current fed into a
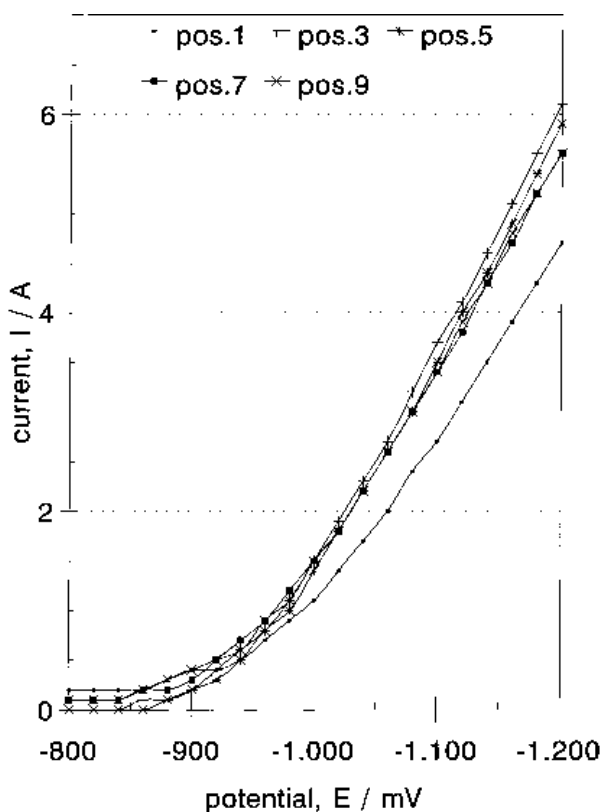
Fig. 2. Voltammograms recorded at single three-dimensional copper electrodes in different positions in the cell (catholyte $2.4 \times 10^{-2} \, \text{mol dm}^{-3}$ Fe^{3+}, $0.23 \, \text{mol dm}^{-3}$ TEA, $0.5 \, \text{mol dm}^{-3}$ NaOH, electrolyte flow 14–$15 \, \text{L min}^{-1}$). Potential vs Ag/AgCl, $3 \, \text{M}$ KCl reference electrode.
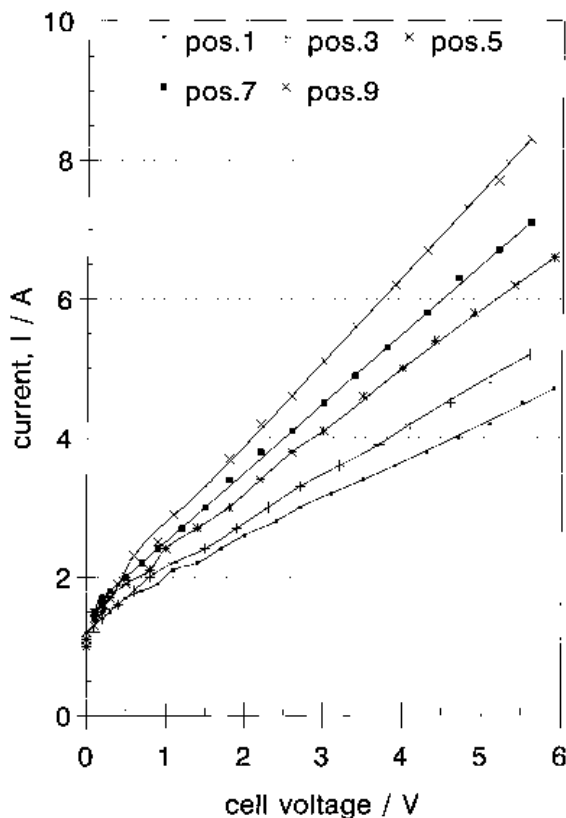
Fig. 3. Cell voltage of single copper cathode units against the current for different electrode positions (catholyte $2.4 \times 10^{-2} \, \text{mol dm}^{-3}$ Fe^{3+}, $0.23 \, \text{mol dm}^{-3}$ TEA, $0.5 \, \text{mol dm}^{-3}$ NaOH, electrolyte flow 14–$15 \, \text{L min}^{-1}$)

single cathode unit against cell voltage is given for different electrode positions. The registered difference in the curves describing the electrode positions arises from the increase in the ohmic resistance in the catholyte due to the increasing distance from the separator.

The curves in Fig. 2 exhibit no significant plateau due to the diffusion limited current, so the maximum current feed into a cathode unit was derived from data given in earlier publications. Voltammograms recorded with a divided cell and plane parallel electrodes exhibit a plateau due to the diffusion limited current density in the height of 4–5 A m^{-2} at a concentration of about 2.4×10^{-2} mol dm^{-3} Fe(III) (mean electrolyte velocity ~2.5×10^{-2} cm min^{-1}) [5].

It can be assumed that not the full surface area of the three-dimensional electrode is working in the diffusion limited region of the current density and a certain increase of the current density is caused by the higher catholyte flow (1.2 cm s^{-1}). Therefore, a mean current density of about 3 A m^{-2} was set as an upper limit for the electrolysis experiments using a single cathode unit in an electrolyte containing 2.4×10^{-2} mol dm^{-3} Fe^{3+}, 0.23 mol dm^{-3} TEA, 0.5 mol dm^{-3} NaOH.

3.2. *Voltage drop within the cathode*

The voltage drop within the cell at different current densities with three inserted cathode units (copper electrodes, sintered glass separator) is given in Fig. 4. The current densities per electrode unit were adjusted at 0.16, 0.33 and 0.5 A m^{-2} (full cell current with three electrode units of 0.5, 1, and 1.5 A).

An increasing voltage drop is caused in the catholyte by the successive addition of the current feed into the electrolyte by the cathodes. The different current density within the catholyte causes an increasing voltage drop in the catholyte. The geometric distances between the cathode units of the cell require

careful optimization to reach a minimum of ohmic losses in the catholyte.

When the ohmic resistance in the catholyte between two cathode units is assumed to be the main factor for a drop in the cell voltage of the cathode units one can calculate the voltage drop and the cell voltage of the different cathode units as a function of the cell current and position of the cathode unit according to Equation 2(a) and (b).

$$U_z = \sum_{i=2}^{k} \Delta U_i \qquad (2a)$$

$$\Delta U_i = RI_o \left(1 - \frac{i-1}{k} \right) \qquad (2b)$$

where U_z is the voltage drop within the cathode, ΔU_i the difference in the cell voltage of the two neighbouring cathode units i and $i-1$, R the ohmic resistance between the two neighbouring cathode units, I_o the current feed in the cathode, and k the number of cathode units.

In Fig. 5 the experimentally determined cell voltage drop in the cathode (copper electrodes) is given for an electrochemical dyestuff reduction using a catholyte containing 7.8×10^{-3} mol dm^{-3} Fe^{3+}, 3.8×10^{-2} mol dm^{-3} TEA, 0.165 mol dm^{-3} NaOH and with addition of 1.9×10^{-2} mol dm^{-3} indigo. The graphs describe the change of the cell voltage within the cathode (10 cathode units) at 5 A and 9 A cell current (0.5 A and 0.9 A per electrode unit, mean current density 0.5 A m^{-2} and 0.9 A m^{-2}) and the cell voltage calculated according to Equation 2 for an electrolyte resistance $R = 0.25 \, \Omega$. The correspondence between the experimentally determined data and the calculated cell voltage is considerable.

Figure 6 shows the cell voltage drop for the stainless steel electrode for cell currents of 2.4, 5.9 and 13 A (current density 0.48, 1.18 and 2.6 A m^{-2}, catholyte 7.8×10^{-3} mol dm^{-3} Fe^{3+}, 4.5×10^{-2} mol dm^{-3} TEA, 0.165 mol dm^{-3} NaOH). The calcu-
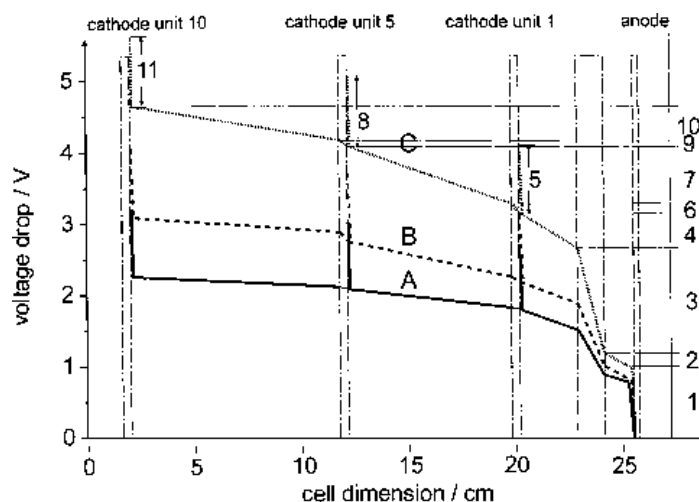

Fig. 4. Voltage drop in the flow through cell (14–15 L min^{-1}) with three copper electrode units (position 1, 5 and 10), at different current densities (A-0.16, B-0.33, C-0.5 A m^{-2}); summary current (A-0.5, B-1.0, C-1.5 A), catholyte 7.8×10^{-3} mol dm^{-3} Fe^{3+}, 4.5×10^{-2} mol dm^{-3} TEA, 0.15 mol dm^{-3} NaOH, anolyte 0.15 mol dm^{-3} NaOH; (1) anode potential, (2) voltage drop in the anolyte, (3) voltage drop in the separator, (4/7/10) voltage drop in the catholyte, (5/8/11) cathode potential, (6/9) voltage drop within the porous cathode.
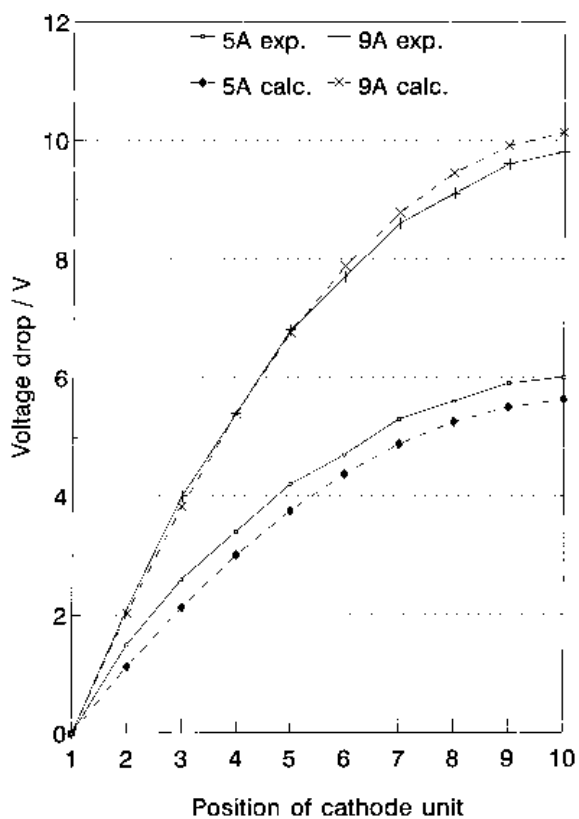
Fig. 5. Voltage drop within a multi-cathode electrode (10 cathode units, copper wire) at 5 and 9 A cell current (catholyte: 7.8×10^{-3} mol dm^{-3} Fe^{3+}, 3.8×10^{-2} mol dm^{-3} TEA, 0.165 mol dm^{-3} NaOH, 1.9×10^{-2} mol dm^{-3} indigo).
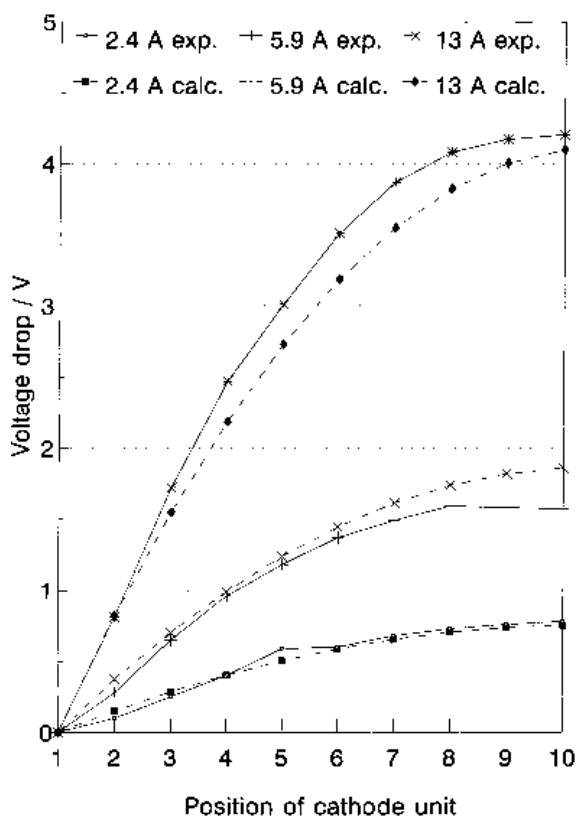

Fig. 6. Voltage drop within a multi-cathode electrode (10 cathode units, stainless steel fabric) at 2.4, 5.9 and 13.0 A cell current (catholyte: 7.8×10^{-3} mol dm^{-3} Fe^{3+}, 4.5×10^{-2} mol dm^{-3} TEA, 0.165 mol dm^{-3} NaOH).

lated values ($R = 0.070$ Ω) are also given in Fig. 6. In the optimized cathode manufactured from stainless steel fabric the spaces between the isolated cathode units were lowered to a great extent from about 0.25 Ω to about 0.070 Ω therefore the loss of cell voltage in the cathode at a current of 10 A was reduced from about 10 V in the copper electrode to less than 4 V in the optimized steel electrode.

The ohmic resistance of the electrolyte (catholyte 2.4×10^{-2} mol dm^{-3} Fe^{3+}, 0.23 mol dm^{-3} TEA, 0.5 mol dm^{-3} NaOH, anolyte 0.5 mol dm^{-3} NaOH, RT) is mainly dependent on the concentration of caustic soda in the mediator solution.

For the technical reduction of dispersed dyestuffs the catholyte must not change the dyeing behaviour of the used dyes so an increase of the conductivity of the catholyte to lower the cell voltage has to be performed in consideration of dyeing experiments [6].

In Fig. 4 it can be seen that the electrode reaction causes a comparable voltage drop at the cathode independent on the current density applied.

A significant part of the voltage drop in the cell proceeds in the ceramic separator due to its ohmic resistance. In the further development of the cell the ceramic separator was replaced by a cation-exchange membrane.

4. Batch electrolysis experiments

4.1. Copper electrodes

The electrochemical efficiency of the electrochemical reactor was determined by series of batch electrolysis experiments in which the concentration of Fe(II)-complex formed was determined by potentiometric titration. An increasing number of electrode units was inserted into the cell and the current efficiency of the cathode was tested in electrolysis experiments. The experimental conditions and the applied current are given in Table 1. In addition the mean current efficiency for a certain part of Fe(II)-complex formed in the catholyte is stated. At a single flow-through electrode a current efficiency of 80–90% at 3 A m^{-2} current density can be reached. The experiments with a low number of electrode units and low total current exhibit an almost constant growth in the Fe(II) concentration up to 70 to 80% turn over. At higher cell current the current efficiency decreases (expts (5) and (6)) although the current density in an electrode unit is lower than in the experiments using three or less electrode units. In the experiment (6) 5 g dm^{-3} indigo were added to the catholyte so in the potentiometric titration of the Fe(II)-complex formed the reduced indigo dyestuff is determined in addition.

To minimize the disturbing influence of dissolved oxygen in the catholyte the starting solution was pre-electrolysed for a duration of about 15 min (in the absence of indigo dyestuff) to achieve a potential in the solution of about −700 mV (vs Ag/AgCl, 3 M KCl). At this potential no significant amounts of Fe(II)-complex are formed in the catholyte.

Table 1. Experimental conditions and results of electrolysis tests with copper wire electrodes (given in Fig. 7).

Catholyte $2.4 \times 10^{-2}\,\text{mol dm}^{-3}$ Fe^{3+}, $0.23\,\text{mol dm}^{-3}$ TEA, $0.5\,\text{mol dm}^{-3}$ NaOH, catholyte volume: 12.5 L (in expt. (6)[*] $1.9 \times 10^{-2}\,\text{mol dm}^{-3}$ oxidized indigo dyestuff was added to the catholyte)

Experiment	Number of cathode units	Cell current /A	Current density /A m^{-2}	Fe(II)-complex formed /%	Mean current efficiency /%
1	1	2–3	2–3	33	79
2	1	3	3	45	94
3	2	5.9	2.9	58	87
4	3	8.8	2.9	54	67
5	10	21	2.1	57	43
6	10	22–26	2.2–2.6	59	78[*]

The power of the cell rises with increasing number of electrodes and increasing total current. At low cell current the direct proportionality between the electrolysis time and the amount of produced Fe(II)-complex is registered but at longer duration of the electrolysis and also at higher sum current a deviation from the ideal behaviour is recorded due to the lowered concentration of reducible Fe(III)-complex in the catholyte.

Table 1 gives experimental conditions of the tests with copper wire electrodes shown in Fig. 7.

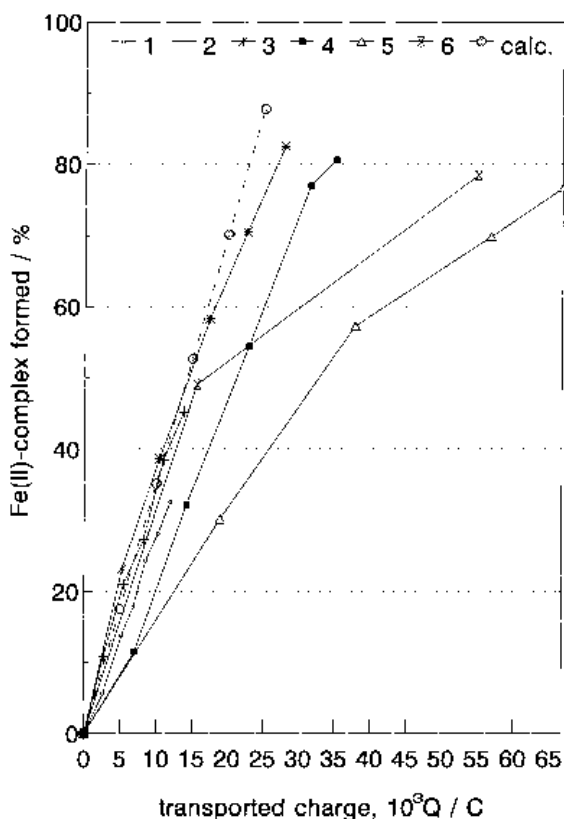As the current density varied somewhat during the experiments the product yield is drawn as a function of the transported charge in Fig. 7. Calculated values for a current efficiency of 100% are also given in Fig. 7.

The formation of reduced species with increasing charge flow easily can be recognised. The linear rise of the concentration of Fe(II)-complex with increasing charge flow proves the good current yield. The slope of the graphs is almost the same up to experiment (4) using three electrode units at a maximum current density of 2–3 A m^{-2} (cell current 8.8 A).

At high cell current (expts (5) and (6) the current efficiency is lowered due to the growing importance of side reactions, for example, evolution of gaseous hydrogen, deposition of elemental iron on the electrode surface.

In addition a bipolar behaviour of the frontier electrode units starts with increased catholyte reduction. A reoxidation of Fe(II)-complexes to Fe(III)-complexes only can be detected when higher concentrations of Fe(II)-complex are present in the catholyte. As the difference in the potential between front and back side of a cathode unit is caused by the current transported in the catholyte flowing through the electrode unit the potential difference between catholyte and cathode changes from the front side of the electrode to the back side of the electrode (compare position 6 and 9 in Fig. 4). This effect is most distinct at the front cathode and at high cell current because the current increases stepwise in the catholyte from the most distant electrode unit to reach a maximum at the electrode nearest the anode. The anodic reaction at the back side of a cathode unit discharges the Fe(II)-complex to the corresponding Fe(III)-complex thus leading to an additional current flowing through a cathode unit causing side reactions on the frontier side of the cathode unit and decreasing the current efficiency.

This effect is influenced by the following parameters: (i) porosity of the electrode (amount of conducting electrolyte in the porous electrode); (ii) thickness of the electrode unit; (iii) conductivity of the catholyte; and (iv) sum current flowing through an electrode unit. An optimization of these parameters has to be done for each investigated electrochemical system.

4.2. Stainless steel cathode units

Copper exhibits a relative high overvoltage for the evolution of hydrogen so this material is favourable for the manufacturing of cathode units. On the other hand the sensitivity of copper to oxidation and dissolution in the alkaline mediator solution whilst no current is fed by the cathodes could cause severe corrosion problems during a stop of the electrochemical cell. Consecutively the copper concentration in the catholyte increases thus leading to environmental problems in technical scale when spent catholyte is released into the wasted water. For that purpose stainless steel was tested as electrode material in an optimization step. Although this material

Fig. 7. Turnover as a function of transported charge (experimental data given in Table 1) for the experiments (1) to (6).

exhibits a lower overvoltage against hydrogen evolution the easy production of electrodes with excellent geometric stability and with low sensitivity to corrosion is favourable. Because of the lower depth of the electrode units and the much enhanced accuracy of the electrode units a remarkable increase in the power of the cell could be achieved, the concentration of the catholyte was lowered and at the same time the current density of the electrode unit was increased. The electrolysis experiments were performed with a cell containing 10 cathode units at a sum current of 5 and 10 A (current per cathode unit 0.5 and 1 A, current density 1–2 A m^{-2}, surface area of one electrode unit 0.5 m^2) using a catholyte containing 7.8×10^{-3} mol dm^{-3} Fe^{3+}, 4.0×10^{-2}–5.4×10^{-2} mol dm^{-3} TEA and 0.15–0.2 mol dm^{-3} NaOH.

In a series of experiments the turnover was determined by a titration of the reduced Fe(II)-complex with 0.1 mol dm^{-3} KMnO$_4$ in acidified solution and the current efficiency were determined for different current densities.

Table 2 gives a survey over the experimental conditions of the tests and the mean current efficiency at a certain turnover.

The experiments were performed at fixed current. In Fig. 8 the turnover is given as a function of electrolysis time and the current efficiency as a function of electrolysis time for typical electrolysis experiments is stated in Table 3.

The results are similar to the data given above for copper electrodes but it must be considered that a drastic increase in the efficiency of the cell could be achieved because the concentration of the Fe(III)-complex has been lowered from 2.4×10^{-2} mol dm^{-3} to 7.8×10^{-3} mol dm^{-3}. In analogy to the experiments with the copper electrodes the current efficiency decreases when Fe(II)-complex is formed in considerable extent. The high current efficiency proves the optimization of the cell construction. Up to a turnover of about 45% Fe(II)-complex the determined current efficiency is 70–80% but rapidly decreases at further increasing concentrations of Fe(II)-complex due to the lowered concentration of reducible species. The apparent low current efficiency at the beginning of the experiments results from the relative slow manual adjustment of the current supply to full cell current. Particularly in the case of low concentrations in the tests with steel electrodes this effect gets more distinct.

5. Conclusions

An electrochemical cell for the indirect cathodic reduction of dispersed indigo with the soluble Fe(III)/Fe(II)–TEA system as mediator requires a cell with

Table 2. Experimental conditions and results of experiments performed with stainless steel cathode units (10 cathode units)

Catholyte volume 12 L

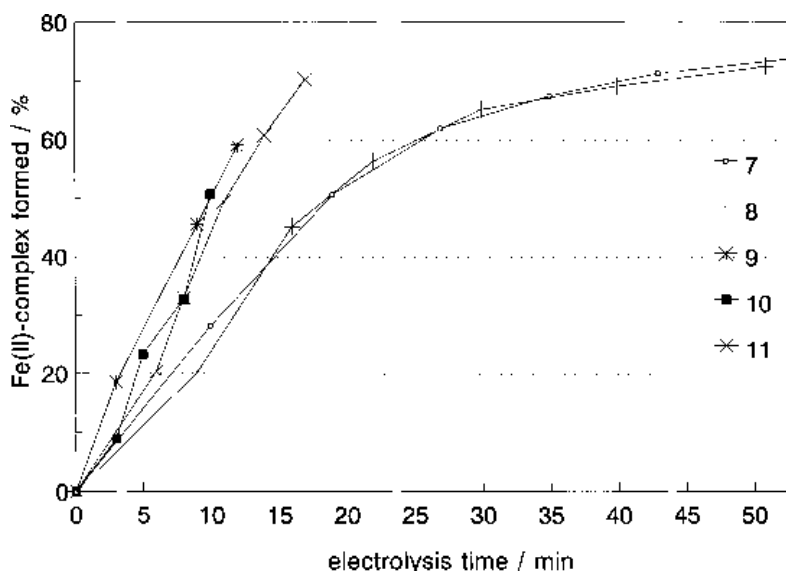| Experiment	Fe / mol dm^{-3}	TEA / mol dm^{-3}	NaOH / mol dm^{-3}	Cell current / A	Current density / A m^{-2}	Fe(II)-complex formed /%	Mean current efficiency /%
7	0.0078	0.053	0.15	5	1	51	78
8	0.0078	0.040	0.15	5	1	57	78
9	0.0078	0.053	0.15	10	2	59	75
10	0.0078	0.040	0.20	10	2	51	77
11	0.0078	0.040	0.15	10	2	50	69

Fig. 8. Turnover as a function of electrolysis time for the experiments (7, 8, 9, 10, 11) given in Table 2.

Table 3. Current efficiency as function of Fe(ɪɪ)-complex formed in electrolysis experiments 7, 8, 9 and 11

Experimental data given in Table 2

Expt. 7		Exp. 8		Exp. 9		Exp. 11	
Fe(ɪɪ) /%	CE /%	Fe(ɪɪ) /%	CE /%	Fe(ɪɪ) /%	CE /%	Fe(ɪɪ) /%	CE /%
28	82	20	68	19	94	20	45
51	73	45	109	46	68	33	95
62	41	57	57	59	69	50	84
68	20	65	33			61	57
71	14	69	12			70	48
74	7	73	9				

high specific electrode area because the current density is limited by the applicable concentration of the mediator in the catholyte. The constructed and tested cell uses up to 10 cathode units which are connected to separately adjustable current supplies. The specific area of an electrochemical reactor is increased by the use of porous flow through electrodes and by the separation of the cathode into several subunits and compensation of the cell voltage drop by separated current supplies. The experimental results prove the successful realization of relative high current densities in the electrolyte.

Starting from a first series of experiments performed with such an electrode the voltage drop at a given cell current within the multi-cathode easily can be calculated with good agreement.

The cathode units were manufactured from copper and in a further optimization from stainless steel. When a solution containing $2.4 \times 10^{-2} \, \text{mol dm}^{-3}$ Fe^{3+}, $0.23 \, \text{mol dm}^{-3}$ TEA, $0.5 \, \text{mol dm}^{-3}$ NaOH was used as catholyte a current efficiency of 70–80% was reached at 2–$3 \, \text{A m}^{-2}$ and 6–$20 \, \text{A}$ cell current with copper electrodes. An optimization of the geometric construction of the electrode units was realized using stainless steel fabric. Thus the electrode units could be manufactured with much enhanced geometric accuracy. The better performance of this construction is proved by the high current efficiency (70–80%) at a current density of $2 \, \text{A m}^{-2}$ with lowered catholyte concentration $(7.8 \times 10^{-3} \, \text{mol dm}^{-3}$ Fe^{3+}, $5.4 \times 10^{-2} \, \text{mol dm}^{-3}$ TEA, $0.15 \, \text{mol dm}^{-3}$ NaOH). The electrolysis experiments were carried out with a cell containing 10 cathode units at a sum current of 5 and 10 A (current density 1 and $2 \, \text{A m}^{-2}$).

The conductivity of the catholyte is coupled to the concentration of the caustic soda and must be regarded as an important parameter for the successful working of the cell with high current efficiency. When larger amounts of Fe(ɪɪ)-complex are produced in the catholyte a discharge and reoxidation to the corresponding Fe(ɪɪɪ)-complex can occur at the backside of the frontier cathode units, particularly at high cell current.

The optimization of the cell construction and the minimization of the mediator concentration is a requirement for the successful realization of the new reduction technique using electrochemically generated Fe(ɪɪ)-complexes in textile dye houses.

Acknowledgement

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