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Electrosynthesis of iminodiacetic acid from nitrilotriacetic acid

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The electrosynthesis of iminodiacetic acid by electrooxidation of nitrilotriacetic acid in undivided cells has been studied using Zn, Cu, PbO_2, DSA®O_2, DSA®Cl_2, C, Ni and porous carbon as anodes. Results show that the synthesis is possible in both acid and basic mediums. The best results were obtained in aqueous 40% w/w sulphuric acid with porous carbon RVC-4000 as anode and SUS 316 as cathode, at 60 °C, 400 mA cm^{-2} and charge 95% of theoretical. Under these conditions, nitrilotriacetic acid conversion was 92%, current efficiency 80% and selectivity 85%. Loss of selectivity was due to chemical side reaction between iminodiacetic acid and HCHO electrogenerated in the electrolysis.

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1. Introduction

Iminodiacetic acid (IDA) is a key intermediate for the synthesis of glyphosate, a broad-spectrum herbicide. There are several methods reported for synthesizing IDA. These are: (i) by catalytic oxidation of diethanolamine [1–3]; (ii) via hydrocyanic acid [4,5]; (iii) by catalytic decarboxylation of nitrilotriacetic acid (NTA) [6]; (iv) by reaction of chloroacetic acid with ammonium [7]; and (v) by electrooxidation of NTA [8, 9].

Method (ii) is currently used in the industry for manufacturing IDA. However, methods (i), (iii) and (v) have potential advantages from environmental and economic standpoints. Consequently, research was undertaken by this company for testing them.

This paper reports a preliminary study carried out at laboratory scale to determine the industrial feasibility of method (v). In this method NTA is electrooxidized in an undivided cell according to the following equation:

$$\underbrace{N(CH_2COOH)_3}_{NTA} + H_2O \xrightarrow{-2e^-} \underbrace{NH(CH_2COOH)_2}_{IDA} + CO_2 + HCHO + 2H^+$$

2. Experimental details

2.1. *Cell design and synthetic procedures*

2.1.1. 10 cm² scale. The preparative electrolysis were carried out at constant current using a Promax FAC-365 (5 A, 30 V) rectifier. A parallel plate, filter press assembly was used as an undivided flow cell with a stainless steel cathode. The electrode area was 10 cm^2 and the interelectrode gap was 5 mm. Polypropylene mesh between the electrodes was used as a turbulence promoter. Electrolyte was contained in a 250 cm^3 jacketed glass reservoir and was pumped through the cell by means of a magnetic pump Iwaki MD-20-R, to provide a flow rate of 2 dm^3 min^{-1}. The reservoir was equipped with a glass filter at the bottom to prevent cell clogging due to undissolved NTA particles, since in some experiments the amount of NTA involved was higher than that permitted by its solubility in the electrolyte. In these cases, the total amount of NTA was added at the beginning of the electrolysis. The undissolved NTA fraction remained above the glass filter and dissolved as the NTA in solution was electrooxidized and, consequently, its concentration in the electrolyte decreased below the saturation value. Temperature was controlled by recirculating water at a specified temperature through the jackets of the reservoir. DSA® electrodes were supplied by Electrocell AB (Sweden) and both graphite JP-845 plate and porous carbon felt RVC-4000 (reticulated vitreous carbon. Specific area (BET) 0.83 m^2 g^{-1}. Electrode area per unit volume 83 000 m^2 m^{-3}) were supplied by Le Carbone Lorraine (France).

2.1.2. 100 cm² scale. The cell was of the same characteristics as described above. The electrolyte reservoir was a 2 dm^3 jacketed glass tank. Pumping was provided by a magnetic pump Iwaki MD-70-R and power was supplied by a 200 A, 25 V rectifier.

2.2. *Analysis*

IDA was analyzed by HPLC at 195 nm using a Perkin–Elmer Chromatograph model 3B, equipped with a u.v. detector (Perkin–Elmer LC-75). The eluent was a solution of monopotassium phosphate 0.084% w/w in methanol (4) : water (96). Its pH was adjusted to 2.5 with phosphoric acid. Flow rate was 2.3 cm^3 min^{-1}. The column was an ion exchange column Spherisorb SAX 10. NTA was analysed by HPLC under the same

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Table 1. Screening experiments for the electrosynthesis of IDA from NTA

NTA concentration: 150 g dm^{-3}; cathode: SUS 316; charge: 60% of theoretical; current density: 100 mA cm^{-2}; temperature: (50–55) °C except for entry 2 (34 °C); amount of NTA involved in each run: 20 g; electrolysis time: 202 min

Entry	*Anode*	*Electrolyte*	*C/%**	*S/%†*	*Ec/%‡*	*V§*
1	PbO_2/Pb	40% w/w H_2SO_4	50	50	41	42.9
2	PbO_2/Pb	40% w/w H_2SO_4	39	59	38	3.1
3	RVC-4000	20% w/w HCl	3	66	2	3.0
4	RVC-4000	40% w/w H_2SO_4	60	88	88	2.2
5**	RVC-4000	40% w/w H_2SO_4	41	91	62	2.5
6	DSA®O_2	40% w/w H_2SO_4	39	79	52	2.4
7	DSA®Cl_2	20% w/w HCl	36	0	0	1.8
8††	Ni	Na_3NTA/H_2O	43	54	38	3.1
9††	Ni	Na_3NTA/10% NaOH	10	0	0	2.1
10††	Ni	Na_3NTA/H_2O	47	7	11	3.2
11††	Cu	Na_3NTA/10%NaOH	23	12	5	2.0
12‡‡	Zn	Na_3NTA/10%NaOH	11	0	0	3.1
13‡‡	RVC-4000	Na_3NTA/H_2O	46	–	–	3.4
14	DSA®O_2	Na_3NTA/H_2O	47	10	8	2.5
15	DSA®Cl_2	Na_3NTA/H_2O/NaCl§§	39	26	17	3.3
16‡‡	RVC-4000	Na_3NTA/H_2O/NaCl§§	–	–	–	3.0
17	DSA®Cl_2	Na_3NTA/H_2O/NaBr§§	36	21	13	3.3

*Conversion; †selectivity; ‡current efficiency; §cell voltage (V); **addition of 14 g dm^{-3} of urea; ††slight anode corrosion; ‡‡strong anode corrosion; §§20 g dm^{-3} of halide.

conditions as IDA except that the eluent pH was adjusted to 1.5. HCHO was quantified by GC by means of a Perkin–Elmer gas chromatograph (model PE-8500) equipped with a TC detector. Two columns in series were used. The first column was a 2.44 m × 0.32 cm, stainless steel Porapack-Q 50/80 mesh column, and the second was a Porapak-R column of the same geometric dimensions. Helium at 40 cm^3 min^{-1} was used as gas carrier. The injector temperature was 175 °C. The column temperature was increased at 12 °C min^{-1} from 25 to 150 °C. The analysis time at 150 °C was 5 min. Sample preparation was carried out by neutralising an aliquot with NaOH to pH 7 and filtering the solution prior to each analysis.

3. Results and discussion

In the following, conversion is the ratio between the amount of NTA electrooxidated and the initial amount of NTA involved in the electrolysis. Selectivity is the ratio between the moles of IDA obtained and the moles of NTA converted.

3.1. *Screening experiments at 10 cm² electrode area*

Initially, a series of experiments was carried out at very different conditions in order to identify conditions favourable to IDA production. The experimental conditions and results obtained are given in Table 1. The best results were obtained when a porous carbon RVC-4000 in 40% w/w sulphuric acid was used as anode. Likewise, promising results were obtained when PbO_2 and DSA®O_2 in sulphuric acid, and nickel in basic medium were used as anodes. In entry 5, 14 g dm^{-3} of urea were added to trap the HCHO produced during the NTA electrooxidation which, as seen later, reacted with IDA, thus decreasing both the faradaic and material yields. This procedure was very effective in the electrosynthesis of glyphosate [10]. However, in this case the result was completely ineffective. Selectivity was slightly higher but the current efficiency decreased dramatically, indicating that electrooxidation of urea was a competitive reaction.

Table 2. PbO_2/Pb anode. NTA concentration: 180 g dm^{-3} in 40% w/w sulphuric acid

Symbols as in Table 1, except for those here specified. Amount of NTA involved in each run: 20 g

Entry	*T/(°C)*	*Q/%**	*D†*	*C/%*	*S/%*	*Ec/%*
1	53	60	100	50	50	41
2	34	60	100	39	59	38
18	65	60	100	23	8	3
19	65	100	100	33	7	2
20	65	100	200	36	0	0

*Charge, % of theoretical.
†Current density, mA cm^{-2}.

Carbon felt RVC-4000, PbO_2, DSA®O_2 and nickel were selected as anodes, and sulphuric acid and an aqueous solution of the trisodium salt of NTA as electrolytes for further study.

The experimental conditions and the results are given in Tables 2 to 5. Initially, 40% w/w sulphuric acid was chosen as electrolyte for experiments carried out in acid medium because the solubility of NTA was sufficiently high (12% w/w at 60 °C) to minimize water electrooxidation.

With PbO_2 as anode the results were poor and not reproducible, probably due to problems related to the reproducibility of the PbO_2 layer structure during its manufacture (it was formed *in situ* on a lead plate by anodic oxidation, at 10 mA cm^{-2} for 20 min in 10% w/w aqueous sulphuric acid, at 25 °C, prior to each experiment). Poor results were also obtained in basic medium with nickel as anode. The use of DSA®O_2 as anode led to relatively good yields, but the best results were achieved when carbon felt RVC-4000 was used as anode. Additional experiments run with nonporous graphite JP-845 plate were completely unsuccessful. A decrease in selectivity ranging from 25 to 50%, depending on the current density, was produced. In

Table 3. Nickel anode. NTA concentration: 180 g dm^{-3} as acid (NTA was used as its trisodium salt). Initial pH 11, final pH 7

Symbols given in Tables 1 and 2. Amount of NTA involved in each run: 20 g

Entry	*T/°C*	*Q/%*	*D*	*C/%*	*S/%*	*Ec/%*
8	50–55	60	100	43	54	38
10	50–55	60	100	47	7	11
21	65	60	100	47	22	17
22	40	60	100	38	12	8
23	40	100	100	58	13	7
24	40	100	200	57	15	8

Table 4. DSA®O_2 anode. NTA concentration: 180 g dm^{-3} in 40% w/w sulphuric acid

Symbols given in Tables 1 and 2. Amount of NTA involved in each run: 20 g

Entry	*T/(°C)*	*Q/%*	*D*	*C/%*	*S/%*	*Ec/%*	*t**
6	50–55	60	100	39	79	52	202
25	40	60	200	33	91	50	101
26	40	90	200	64	66	47	151.5
27	40	90	300	55	61	37	101
28	40	100	300	60	76	46	112
29	50–55	60	200	60	76	55	101

*Electrolysis time, min

addition, the anode was seriously corroded. Consequently, carbon felt RVC-4000 and aqueous sulphuric acid were chosen as anode and electrolyte, respectively, for optimization studies.

3.2. *Optimization: porous carbon felt RVC-4000 anode*

The influence of the initial concentration of NTA is given in Fig. 1. Both current efficiency and conversion increase with NTA concentration. In contrast, the higher the NTA concentration, the lower the selectivity. Taking into account that the NTA current efficiency is close to 100% above 300 g dm^{-3}, the decrease of selectivity cannot be related to IDA electrooxidation, but to a chemical side reaction between IDA and another species.

HCHO is synthesized as byproduct during the electrolysis, and probably reacts easily with IDA. In fact, in an experiment in which IDA was reacted with HCHO at 60 °C in 40% w/w sulphuric acid for 2 h, an IDA conversion of 15% was produced. In another experiment, 25% w/w IDA in 20% w/w sulphuric acid was reacted at 60 °C with HCHO (5.64% w/w, 1 mol IDA : 1 mol HCHO). After 24 h, 17% of IDA was converted to an unidentified product (probably *n*-methylol iminodiacetic acid).

The increase in the NTA concentration gives rise to two effects: on one hand, to an increase in the electrolysis time because all the electrolysis were ended when 90% of theoretical charge was passed, and, on the other hand, to an increase of the IDA concentration. Both parameters favour IDA–HCHO condensation, producing the decrease of selectivity observed.

Table 5. Porous carbon RVC-4000 anode. NTA concentration: 180 g dm^{-3} in 40% w/w sulphuric acid

Symbols given in Tables 1 and 2. Amount of NTA involved in each run: 20 g

Entry	*T/(°C)*	*Q/%*	*D*	*C/%*	*S/%*	*Ec/%*	*t**
4	50–55	60	100	60	88	88	202
5†	50–55	60	100	41	91	62	202
30	40	60	100	60	100	100	202
31	40	90	100	84	96	90	303
32	40	90	200	86	96.5	92	151.5
33	40	90	300	86	95	90	101
34	25	90	200	75	79	66	151.5
35	27	90	500	40	59	26	60.6
36	28	95	300	86	85	77	106.5
37‡	45	90	200	88	93	90	151.5

*Electrolysis time, min.

†Addition of 14 g dm^{-3} of urea.

‡Electrolyte: 20% w/w sulphuric acid.

The influence of temperature is given in Figs 2 and 3 for two different initial NTA concentrations. For each NTA concentration there is an optimum temperature which increases when the NTA concentration increases. Nevertheless, above 50 °C, the selectivity is practically constant. The influence of the current density, sulphuric acid concentration and charge is given in Figs 4, 5 and 6, respectively. Selectivity and conversion are practically independent of current density, except for low temperatures. For low NTA concentrations, yields are independent of sulphuric acid concentration. On the contrary, for high NTA concentrations both selectivity and conversion increase sharply as sulphuric acid concentration increases. For low NTA concentrations, conversion decreases sharply above 85% of theoretical charge. For high concentrations, neither selectivity nor conversion depend on charge.

3.3. *Experiments at 100 cm^2 electrode area*

According to the results achieved at 10 cm^2 scale, the following conditions were chosen:

NTA concentration: 540 g dm^{-3}
Electrolyte: 40% w/w sulphuric acid
Charge: 95% of theoretical
Anode: carbon felt RVC-4000
Current density: 400 mA cm^{-2}
Temperature: 60 °C

In these conditions, the following results were obtained:

Conversion: 90%
Current efficiency: 81%
Selectivity: 85%
Final IDA concentration: 287 g dm^{-3}
Specific productivity: 8 kg h^{-1} m^{-2}
Mean voltage: 4.5 V
Power consumption: 2.25 kW h kg^{-1}

Working at a NTA concentration below 200 g dm^{-3} a selectivity of 100% could be obtained (see Fig. 1). However, a higher NTA concentration was chosen to obtain a final IDA concentration sufficiently high to facilitate its isolation.

Experiments at this scale were exclusively undertaken to test both the performance of the cathode and the influence of the side reaction between IDA and HCHO on a larger scale. The influence of the flow rate was not specifically studied. A flow rate sufficiently high to obtain good mass transfer was chosen. The minimum value was determined by monitoring the cell voltage. When the flow rate was not sufficiently high for good mass transfer, the cell voltage increased sharply. Thus, with the 100 cm^2 cell, the flow rate was 5.75 dm^3 min^{-1} (linear velocity: 24 cm s^{-1}).

Porous carbon anodes on the 100 cm^2 scale were

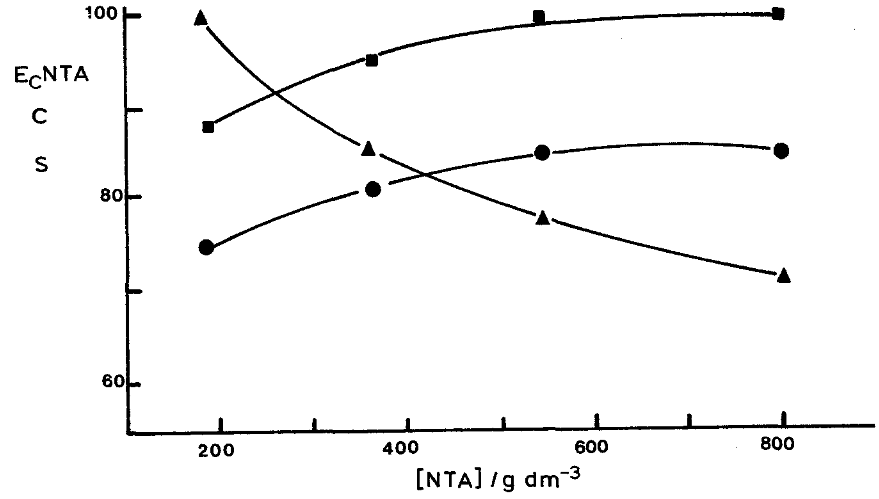

Fig. 1. Influence of initial NTA concentration on conversion (*C*/%), NTA current efficiency (*Ec*NTA/%) and selectivity (*S*/%), Anode: porous carbon RVC-4000; cathode: SUS 316; electrolyte: 40% w/w sulphuric acid: current density: 300 mA cm^{-2}; *T*: 50 °C; charge: 90% of theoretical; electrolysis time: 112 min for 200 g dm^{-3}; 448 min for 800 g dm^{-3}. (●) Conversion, (■) *Ec*NTA, (▲) selectivity.

designed in the same way as for the 10 cm^2 scale: the porous carbon felt RVC-4000 was supported by pressure on a plate of JP-845 graphite which acted as current feeder. The JP-845 plate was perforated and the electrolyte was pumped through the cell from behind the JP-845 face in contact with the porous carbon.

Three experiments were run under the conditions given above. Conversion decreased by 25% and selectivity by 20%. After dismantling the cell, the JP-845 support was heavily corroded, indicating that, on this scale, the contact between porous carbon and its JP-845 plate support was not intimate.

To overcome this problem, the anode was redesigned. A felt of porous carbon RVC-4000 (thickness: 5 mm) was sandwiched between two graphite JP-845 plates (height: 190 mm, width: 100 mm, thickness: 5 mm each) in such a way that a window of 100 cm^2 porous carbon was formed at the centre of the electrode. The electrolyte passed through this window and practically no part of the graphite JP-845 was in contact with it. Both graphite JP-845 plates were sealed with graphite AN concrete (Le Carbone-Lorraine).

Using this electrode, an electrolysis was run under the above mentioned conditions. The results were:

Conversion: 87.5%

Current efficiency: 62.0%

Selectivity: 68.5%

The mean cell voltage was 4 V. The anode was not corroded. Conversion was close to the expected. However, selectivity decreased by 16.5%. Taking into account that the NTA current efficiency was 91%, the decrease in selectivity can only be explained if IDA reacts with the HCHO formed as byproduct. Apparently, scale up produced conditions which enhanced IDA-HCHO condensation.

4. Conclusions

At present, electrosynthesis of IDA from NTA is not a competitive route in comparision with the catalytic oxidation of diethanolamine from both economic and technical points of view.

Further effort is necessary to improve the performance of the electrolytic route. Attention should be focused on the anode design and on finding conditions

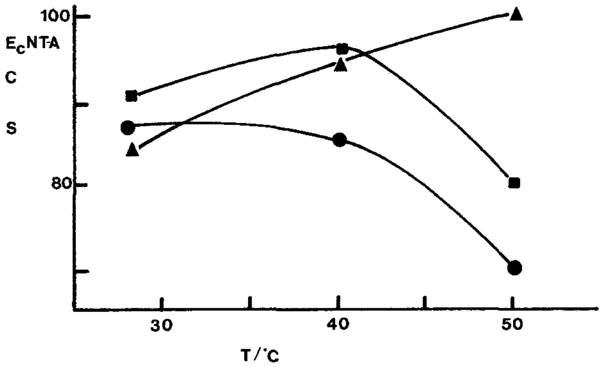

Fig. 2. Influence of temperature on conversion (*C*/%), NTA current efficiency (*Ec*NTA/%) and selectivity (*S*/%). Anode: porous carbon RVC-4000; cathode: SUS 316; electrolyte: 40% w/w sulphuric acid; NTA concentration: 180 g dm^{-3}; current density: 300 mA cm^{-2}; charge: 90% of theoretical; electrolysis time: 10 min. (●) Conversion, (■) *Ec*NTA, (▲) selectivity.

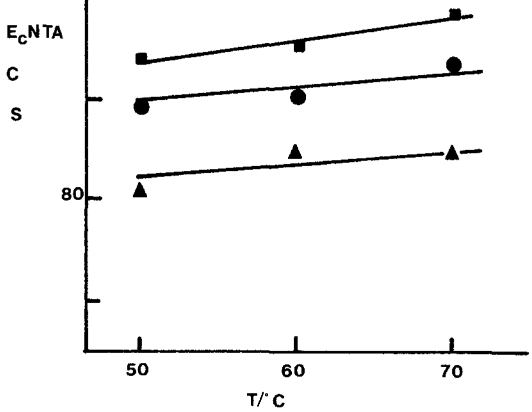

Fig. 3. Influence of temperature on conversion (*C*/%), NTA current efficiency (*Ec*NTA/%) and selectivity (*S*/%). Experimental conditions as in Fig. 2, except that charge: 95% of theoretical, NTA concentration: 540 g dm^{-3}. Electrolysis time: 320 min. (●) Conversion, (■) *Ec*NTA, (▲) selectivity.

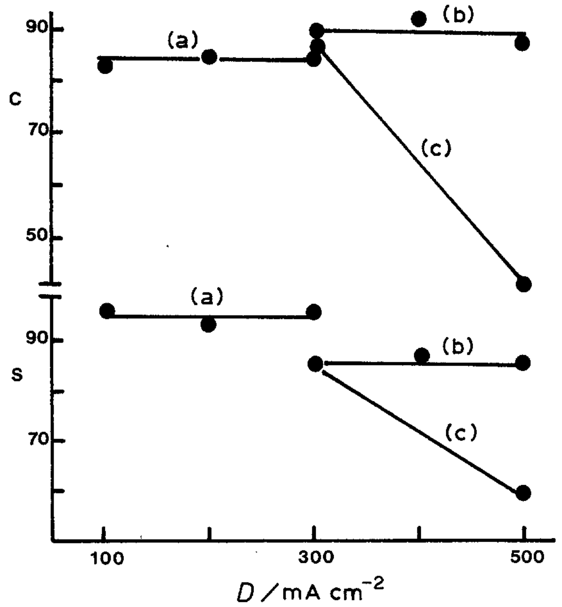

Fig. 4. Influence of current density (D) on conversion (C/%) and selectivity (S/%). Anode: RVC-4000. Cathode: SUS 316. Electrolyte: 40% w/w sulphuric acid. (a) 40 °C, 90% of theoretical charge, NTA concentration 180 g dm^{-3}. Electrolysis time: 303 min for 100 mA cm^{-2}; 60.6 min for 500 mA cm^{-2}. (b) 60 °C, 95% of theoretical charge, NTA concentration 540 g dm^{-3}. Electrolysis time: 500 min for 100 mA cm^{-2}; 320 min for 300 mA cm^{-2}; 192 min for 500 mA cm^{-2}. (c) 27 °C, 90% of theoretical charge, NTA concentration 180 g dm^{-3}. Electrolysis time as given in (a).

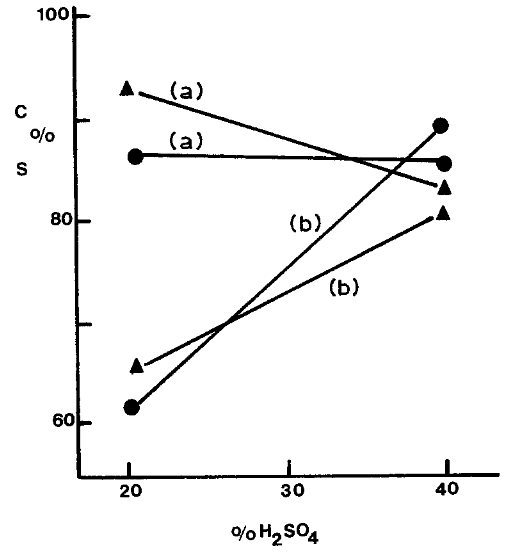

Fig. 5. Influence of sulphuric acid concentration. (a) 40 °C, 90% of theoretical charge, 200 mA cm^{-2}, NTA concentration: 180 g dm^{-3}. Electrolysis time: 151.5 min. (b) 50 °C, 95% of theoretical charge, 300 mA cm^{-2}, NTA concentration: 540 g dm^{-3}. (●) Conversion, (▲) selectivity.

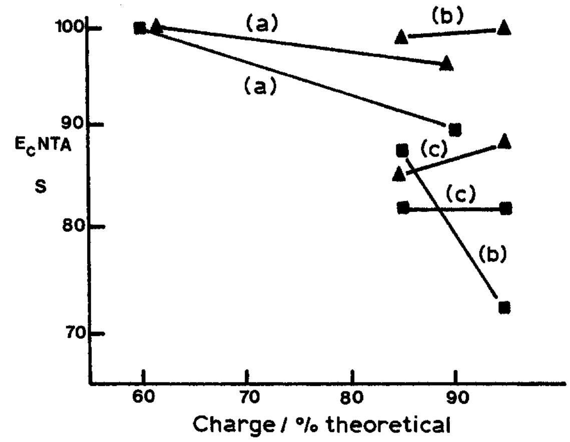

Fig. 6. Influence of charge. Anode: RVC-4000. Cathode: SUS 316 Electrolyte: 40% w/w sulphuric acid. (a) 40 °C, 100 mA cm^{-2}, NTA concentration 180 g dm^{-3}. Electrolysis time: 202 min for 60% of theoretical charge. (b) 50 °C, 300 mA cm^{-2}, NTA concentration 180 g dm^{-3}. Electrolysis time: 106.6 min for 95% of theoretical charge. (c) 50 °C, 300 mA cm^{-2}, NTA concentration 360 g dm^{-3}. Electrolysis time. 191 min for 85% of theoretical charge. (■) *Ec*NTA, (▲) selectivity.

which eliminate IDA–HCHO condensation. Study of this chemical reaction will facilitate the improvement of the electrolytic reaction.

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