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固定床反应器电合成乙醛酸的研究

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摘要: 以过饱和草酸水溶液为阴极液, 盐酸为阳极液, 在固定床电解槽中草酸电还原得到乙醛酸. 考察改变固定床的结构、电解温度及电流密度对生成乙醛酸电流效率和产率的影响. 结果表明, 以铅粒作阴极, 石墨板作阳极, 电流密度 $96.3 \text{ A} \cdot \text{m}^{-2}$, 阴极液空速 $0.505 \text{ m} \cdot \text{s}^{-1}$, 电解温度 32°C 时, 在固定床双阳极室内反应 45 min , 乙醛酸的电流效率仍达到 66.2% , 浓度 2.02% .

关键词: 固定床; 草酸; 电合成; 乙醛酸

中图分类号: TQ 151.5

文献标识码: A

乙醛酸是最简单的醛酸, 兼具醛和酸的两种性质, 可作为香料、医药、农药、油漆、氨基酸精细化工产品的中间体; 还可用于水性涂料、表面活性剂、食物储存及高分子合成交联剂, 是一种具有较好发展前途的精细化工产品原料. 最近二十多年来, 世界各地陆续开发出多种方法生产乙醛酸, 但从经济技术和环保角度分析, 电化学合成法的长处不言而喻. 其中, 草酸电还原法因其具有原料易得、工艺流程简短、产品收率高和纯度好等许多优点而引起广泛关注^[1~7], 但至今的工艺研究均集中于平行板反应器, 而有关的固定床电合成法则未见报道. 由于草酸在水中的溶解度较小, 本身又是较弱电解质, 导电能力差, 使得该电解过程无法在较高浓度和较大的电流密度下进行, 因而设备时空产率甚低. 为此, 若能在平行板反应器基础上, 进一步对固定床草酸电合成乙醛酸进行研究, 将具有极其重要的理论意义和经济价值.

1 实验

采用聚氯乙烯板制成双阳极室和单阳极室两种电解槽, 阴、阳两极室之间隔有强酸型阳离子交换膜. 阴极有效尺寸 $22 \text{ mm} \times 21 \text{ mm} \times 140 \text{ mm}$, 材料: 铅粒或石墨粒, 平均粒径 2.6 mm , 阴极床层空隙率为 0.375 , 外表面积约为 0.0623 m^2 , 阴极液空速为 $0.505 \text{ m} \cdot \text{s}^{-1}$; 阳极两个, 材料: 石墨板, 尺寸: $22 \text{ mm} \times 5 \text{ mm} \times 140 \text{ mm}$.

图1是实验流程图, 于阴极槽装入 200 mL 过饱和草酸溶液, 阳极槽中盛 13.3% (wt %) 的盐酸溶液, 通过控温系统调节温度, 每隔一段时间取样一次, 分析其中的乙醛酸含量. 分析方法参见文献[8~9].

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2 实验结果与讨论

2.1 电解槽的选择

分别以单阳极室和对称双阳极室两种电解槽进行实验. 结果如表 1.

从表 1 数据可知, 相同电流密度和电解时间下, 双阳极室固定床电解槽的电流效率和时空产率均比单阳极室高. 究其原因可能是对称双阳极室固定床反应器中径向传质均匀, 浓度分布均匀, 从而电流分布也均匀, 对反应有利. 故本文选用对称双阳极室作进一步研究.

2.2 阴极材料的选择

选用对称双阳极室, 分别以铅粒和石墨粒作阴极, 实验结果如表 2.

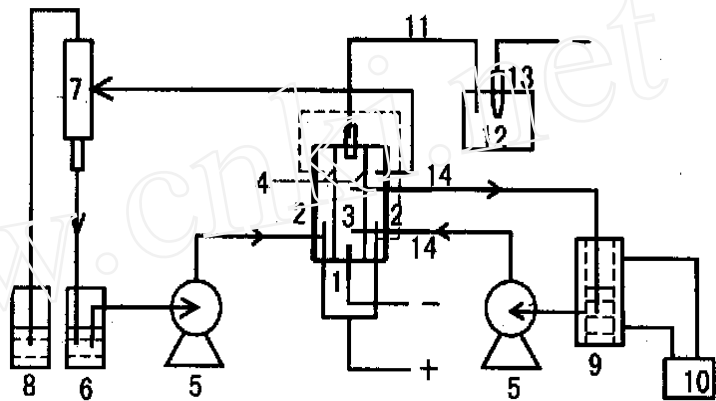


图 1 固定床反应器电合成乙醛酸实验流程图

Fig. 1 Experimental apparatus for electro-synthesis of glyoxylic acid in a packed bed reactor

- (1) electrolysis cell (2) anode of graphite board (3) cathode of packed bed (4) ion-exchange membrane (5) pump (6) hydrochloric acid aqueous vessel (7) gas-liquid separator (8) gas-sorption cell (9) oxalic acid aqueous vessel (10) thermostatical water bath (11) salt-bridge (12) saturated potassium chloride aqueous (13) calomel electrode (14) thermoelectric couple

表 1 单/双阳极室电解槽乙醛酸浓度和电流效率比较

Tab. 1 Concentration of glyoxylic acid and current efficiency in a single/ double-anode cell ($T = 26 \sim 29$)

$i / A \cdot m^{-2}$	t / min	Concentration of glyoxylic acid		Current efficiency	
		W / (%)		/ (%)	
		single	double	single	double
16.1	5	0.039	0.040	62.1	69.0
	15	0.083	0.100	48.0	57.8
	30	0.147	0.154	42.7	44.5
	45	0.179	0.188	34.6	36.3
48.2	5	0.109	0.139	66.9	80.5
	15	0.242	0.307	48.8	59.4
	30	0.426	0.451	43.1	45.6
	45	0.610	0.625	39.3	40.4
80.3	5	0.216	0.267	68.6	92.9
	15	0.502	0.645	58.3	80.3
	30	1.01	1.22	54.9	66.1
	45	1.35	1.69	50.5	65.4

表 2 不同阴极材料乙醛酸浓度和电流效率比较

Tab. 2 Concentration of glyoxylic acid and current efficiency under different electrode materials

T/	$i / \text{A} \cdot \text{m}^{-2}$	t/ min	W/ (%)		/ (%)	
			graphite	lead	graphite	lead
26	48.1	15	0.247	0.307	47.8	59.4
		30	0.406	0.451	39.2	45.6
30	96.3	15	0.672	0.959	64.9	84.1
		30	0.913	1.395	44.2	68.5

由上表可知,在相同的条件下,石墨粒的电流效率和时空产率均比铅粒差.因此,我们的实验体系选择铅粒作为阴极材料.

2.3 温度的影响

选用对称双阳极室,改变并控制进料草酸的温度,考察了电解温度对乙醛酸浓度和电流效率的影响.表 3 结果表明,低温对草酸电还原合成乙醛酸有利,温度升高时电流效率和产率均下降,且超过 20 后急剧下降.这是因为草酸的还原反应为放热反应,当反应温度升高且超过一定值后,将降低乙醛酸的最终生成速率,有利于生成乙醇酸副反应的进行^[2],导致电流效率和产率下降.

表 3 不同温度下乙醛酸浓度和电流效率的比较

Tab. 3 Concentration of glyoxylic acid and current efficiency under different temperatures ($i = 16.1 \text{ A} \cdot \text{m}^{-2}$)

T/	t/ min	W/ (%)	/ (%)
21	5	0.053	92.7
	15	0.201	87.5
	30	0.250	72.4
	45	0.355	68.6
26	5	0.040	69.0
	15	0.100	57.8
	30	0.154	44.5
	45	0.188	36.3
29	5	0.039	68.1
	15	0.086	47.7
	30	0.128	33.9
	45	0.164	31.7

2.4 电流密度的影响

选用对称双阳极室,改变并控制反应的电流,考察了电流密度对电合成乙醛酸浓度和电流效率的影响,实验结果如表 4.增大电流密度可以提高生产强度,但电流密度过高势将导致电极电位偏离最佳范围,副反应加剧,电流效率下降.由实验结果可知,本实验电流密度以 96.3

~ 117.2 A · m⁻²之间为宜.

表 4 不同电流密度下乙醛酸浓度和电流效率的比较

Tab. 4 Concentration of glyoxylic acid and current efficiency under different current densities($T = 29 \sim 32$)

$i / \text{A} \cdot \text{m}^{-2}$	t / min	$W / (\%)$	$\eta / (\%)$
80.3	5	0.257	92.9
	15	0.645	80.3
	30	1.22	66.1
	45	1.69	65.4
96.3	5	0.734	96.7
	15	0.959	84.1
	30	1.40	68.5
	45	2.02	66.2
117.2	5	0.764	97.5
	15	1.02	84.8
	30	1.62	65.6
	45	2.10	55.7

3 结 语

1) 用铅粒做阴极,石墨板做阳极,电流密度 96.3 A · m⁻²,空管流速 0.505 m · s⁻¹,电解温度 32 ℃ 时,在固定床双阳极室内反应 45 min,乙醛酸电流效率仍达到 66.2%,乙醛酸的浓度为 2.02%。研究的初步结果表明,该技术时空产率高,上述条件下时空产率达 0.11 Kg · dm⁻³ · h⁻¹以上,适当降低电解温度可望反应 1.5 h 内达到乙醛酸 4% 的出料要求。而据平行板反应器的一般报道^[7,10~11],反应 3.5~8 h 也只达到 4.54%~7.81% 的出料浓度。因此本文提出的固定床反应器为草酸电还原生成乙醛酸提供了一种合理的新途径。

2) 草酸阴极还原放热量很大,高电流密度时本反应器往往即刻升温约有 10 ℃。对高电流密度的反应,如电解温度太高,将导致副反应加大,电流效率下降快。如何快速移走热量是本固定床工业化的瓶颈问题。我们正在积极改进装置,以实现高电流且较低温度(20 ℃ 以下)的操作。

Electrosynthesis of Glyoxylic Acid in a Packed Bed Reactor

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Abstract: Glyoxylic acid was produced by electroreduction of oxalic acid in a packed bed

reactor. The cathodic and anodic electrolytes were super-saturated oxalic and hydrochloric acid aqueous solutions separated by a super-acid ion-exchange membrane. The current efficiency and yield of glyoxylic acid were studied under different structured packed bed reactors and different electrode materials, temperatures and current densities. The results indicated that the current efficiency of synthesis of glyoxylic acid was over 66.2% and the concentration of glyoxylic acid could reach 2.02% after 45min electrolysis with cathode of lead particles and anode of graphite board under conditions of temperature 32℃, superficial flow rate of $0.505 \text{ m} \cdot \text{s}^{-1}$ and current density of $96.3 \text{ A} \cdot \text{m}^{-2}$ in a packed bed reactor with double-anode cell.

Key words: Packed bed, Electrolysis, Oxalic acid, Glyoxylic acid

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