

2009-05-28

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Recommended Citation

Hao SHEN, Jin-hong FAN, Lu-ming MA. Investigation on Electrogenerated Active Chlorine from diluted NaCl Solutions at Ti/Pt Anode[J]. *Journal of Electrochemistry*, 2009 , 15(2): 220-223.

DOI: 10.61558/2993-074X.1984

Available at: <https://jelectrochem.xmu.edu.cn/journal/vol15/iss2/19>

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低浓度 NaCl 溶液 Ti/Pt 阳极电解制备活性氯

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摘要: 以 Ti 板阴极、Ti/Pt 阳极组成无隔膜电解装置, 电解低浓度 NaCl 溶液制得活性氯. 研究电解时间、电流密度、氯离子浓度、溶液 pH 值对活性氯浓度及电流效率的影响. 结果表明: 电解时间增加, 活性氯浓度增加, 而电流效率逐渐降低; 初始阶段活性氯浓度增加较快, 近 1 h 活性氯浓度趋于稳定; 增加氯化钠浓度可提高活性氯浓度和改善电流效率; 微酸性电解液有利于提高活性氯浓度. 电解过程中, 溶液电导率不断降低, pH 值变化范围在 1 之内.

关键词: 活性氯; Ti/Pt 阳极; 低浓度 NaCl 溶液; 电解

中图分类号: TQ151.2⁺; X703.1; O646.51 **文献标识码:** A

活性氯主要成分有氯气、次氯酸和次氯酸盐, 广泛用于饮用水、食品饮料、下水道污水的消毒. 活性氯通常由电解低浓度氯化钠溶液制得. 文献已有报道利用电解 NaCl 去除染料^[1]、甲酚^[2]、氯酚^[3-4]、生产消毒剂^[5-7]或用作生活污水处理^[8].

本文以 Ti/Pt 阳极、Ti 阴极组成单室电解装置, 电解低浓度 NaCl 溶液, 研究电流密度、氯离子浓度、电解液 pH 值对活性氯的影响, 为污水厂二沉池出水的深度处理, 生物性污染物和低浓度 COD_{Cr}、TP、NH₃-N 污染物的去除提供实验依据.

1 试验部分

去离子水配制测试溶液, 分析活性氯^[6,9]采用 N,N-二乙基-1,4-苯二胺分光光度法 (GB11898-89).

2 结果与讨论

2.1 电解时间

图 1 示出: 在电流密度为 9.85 mA/cm^2 下, 活性氯浓度、电流效率随电解时间变化. 电解时间延长, 活性氯浓度增加, 电流效率降低; 电解时间近 1 h 活性氯浓度趋于稳定, 故电解时间选取 1 h 为宜.

在 Bechtold^[10]的研究中也出现类似结果, 这可能是 ClO^- 在阴、阳极发生副反应所致.

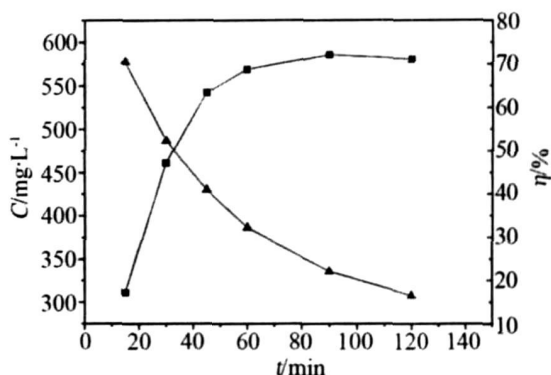


图 1 活性氯浓度、电流效率随电解时间变化曲线 (电解液 1 g/L NaCl 溶液)

Fig 1 Variations of the active chlorine concentration and current efficiency with electrolysis time at 9.85 mA/cm^2

2.2 电流密度

图 2~5 分别示出不同电流密度对活性氯浓度、电流效率、溶液电导率和溶液 pH 值的影响. 从图 2 看出, 活性氯浓度均随电解时间延长而升高, 7.39 、 9.85 mA/cm^2 下, 二者活性氯浓度曲线几乎

重叠,表明在较高电流密度下活性氯生成速率趋向恒定^[11].

由图 3 可知,电流效率随电流密度增加而降低,电解初期 4.93 mA/cm^2 的电流效率反而低于 7.39 mA/cm^2 的.这可能在稀 NaCl 溶液中,氯离子含量低,加大电流密度析氧反应加快,导致电流效率下降,活性氯生成速率减慢^[12];较高电流密度下电解,将出现浓度极化,此时析氯电流效率不再提高^[13];同时由于副反应 ClO_3^- 的积累而增多,电流效率加速降低.

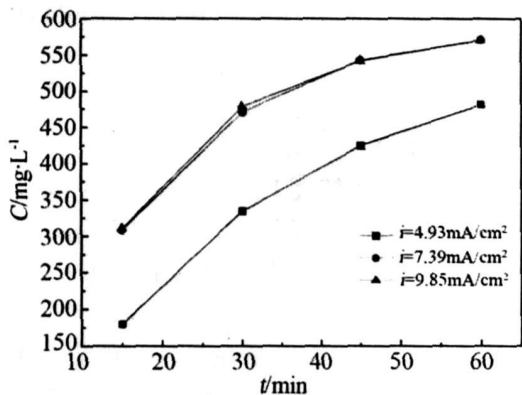


图 2 活性氯浓度随电解时间变化
Fig. 2 Variations of the active chlorine concentration with electrolysis time (electrolyte: 1g/L NaCl solution)

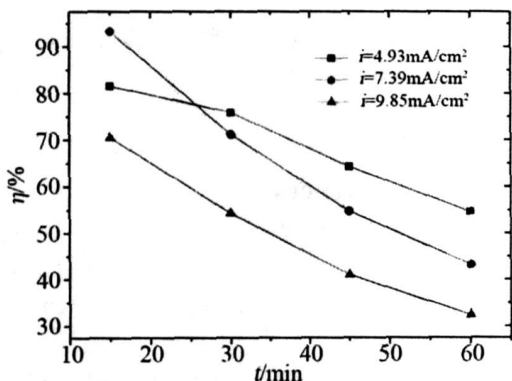


图 3 电流效率随电解时间变化(电解液 1 g/L NaCl 溶液)
Fig. 3 Variations of the current efficiency with electrolysis time (electrolyte: 1g/L NaCl solution)

图 4 显示电解过程溶液电导率不断降低,电流密度越高,电导率下降越快.这可能是电解过程阴阳极产生大量气泡,并形成气液混合体系,致使电导率下降,能耗增加.而气泡也促进电解液对流,加快传质过程.

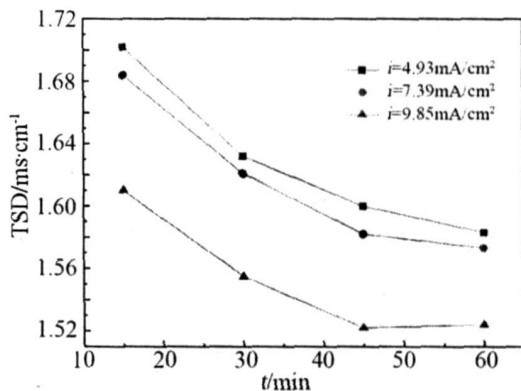


图 4 溶液电导率随电解时间变化
(电解液 1g/L NaCl 溶液)
Fig. 4 Variations of electrolyte's conductivity with electrolysis time (electrolyte: 1g/L NaCl solution)

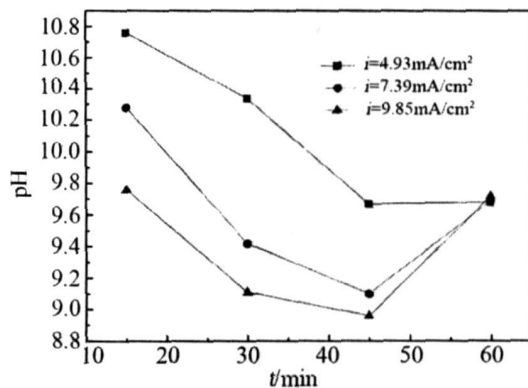


图 5 溶液 pH 随电解时间变化(电解液 1g/L NaCl 溶液)
Fig. 5 Variations of pH with electrolysis time (electrolyte 1 g/L NaCl solution)

从图 5 看出,在不同电流密度下,电解液 pH 值均随电解时间迅速升高,尔后降低,继而再升高.初步解析可认为,反应初始时产生大量 Cl_2 和 OH^- ,电解液 pH 值升高,随电解时间延续,最后几乎达到同一 pH 值. Cl_2 可产生 ClO^- ,消耗了溶液中的 OH^- , ClO^- 又可在阳极释放出 H^+ , OH^- 还可在阳极消耗析出氧气,阴极 OH^- 难以及时补充,因此 pH 值降低.阴极不断析出 H_2 还需消耗 H^+ , pH 在电解 45 min 后又升高,最终溶液都达到几乎相同的平衡点.

2.3 氯离子浓度

氯离子浓度增加可以减少阳极析氧副反应,提高析氯效率,使活性氯浓度增大.如图 6 所示, Cl_2 浓度增加,活性氯浓度也增加,但增幅下降.

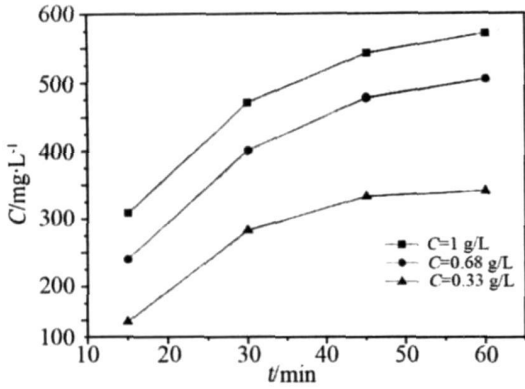


图 6 C_{NaCl} 对活性氯的影响 ($i=7.39\text{mA}/\text{cm}^2$)
Fig 6 Effect of C_{NaCl} on active chlorine concentration ($i=7.39\text{mA}/\text{cm}^2$)

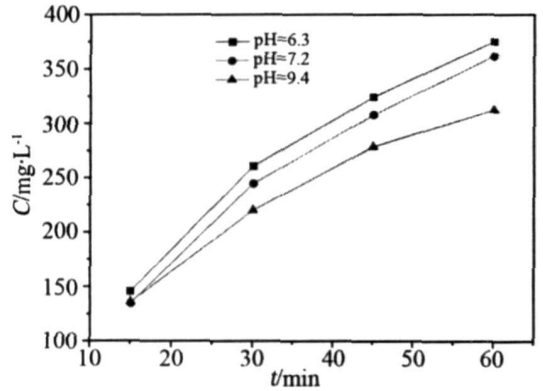


图 7 C_{NaCl} 对电流效率的影响 ($i=7.39\text{mA}/\text{cm}^2$)
Fig 7 Effect of C_{NaCl} on current efficiency ($i=7.39\text{mA}/\text{cm}^2$)

如图 7, C_{NaCl} 增加,可大幅提高电流效率.这与 $Q_{in}^{[5]}$ 在 $C_{NaCl} > 10\text{g/L}$ 溶液电解所得的结论一致.

2.4 pH 值

图 8 示明电解液 pH 值 (6.3、7.2、9.4)对活性氯浓度的影响.微酸性电解液更有利于提高活性氯浓度.

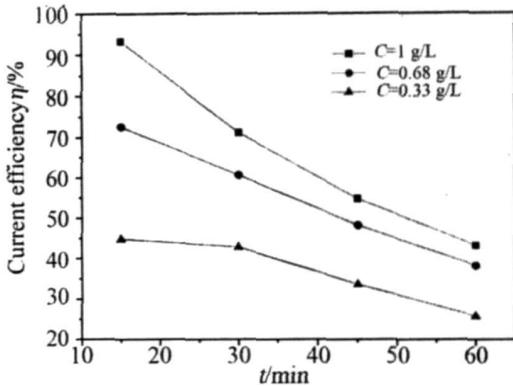


图 8 电解液 pH对活性氯浓度的影响 ($i=7.39\text{mA}/\text{cm}^2$)
Fig 8 Effect of pH on active chlorine concentration
 $i=7.39\text{mA}/\text{cm}^2$, $\text{Na}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ buffer solution
pH: 6.3, 7.2, 9.4

低浓度 NaCl 溶液,氯气生成量小,在微酸性溶液生成 Cl_2 几乎可完全溶解生成 HClO ,降低 ClO^- 发生副反应的可能.若为碱性溶液,则阳极析 O_2 增加,析 Cl_2 的电流效率降低,其活性氯主要以 ClO^- 形式存在,且 ClO^- 分别在阳阴极生成 ClO_3^- 和 Cl^- ,使活性氯浓度降低.当 pH 值在 6~8 时, HClO 与 ClO^- 共存.

3 结 论

1)氯化钠溶液浓度 1g/L ,电流密度 $9.85\text{mA}/\text{cm}^2$ 下,随着电解时间延续,活性氯浓度增加,电流效率逐渐降低;并且初始阶段活性氯浓度速率增加较快,电解近 1h 活性氯浓度趋于稳定.

2)氯化钠溶液浓度为 1g/L 时,电流密度由 $4.93\text{mA}/\text{cm}^2$ 增至 $7.39\text{mA}/\text{cm}^2$,电解 1 h 产生的活性氯浓度升至 100mg/L 继续延长电解时间,活性氯浓度不再增加;增加氯化钠浓度可提高活性氯浓度和改善电流效率;微酸性电解液更利于提高活性氯浓度.

3)电解过程,溶液电导率不断降低, pH 值变化范围在 1 之内.

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Investigation on Electrogenerated Active Chlorine from diluted NaCl Solutions at Ti/Pt Anode

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Abstract: Electrogeneration of active chlorine from diluted NaCl solutions was investigated in an undivided cell with Ti/Pt anode and Ti plate cathode. The effects of electrolysis time, current density (i), chloride concentration and pH value on the electrogeneration of active chlorine and current efficiency (CE) were analyzed. Meanwhile, the changing trends of the electrolyte's conductivity (TSD) and pH value in the electrolysis process were discussed. The results showed that the concentration of active chlorine increased with electrolysis time, but the trend became slow. During this process, the current efficiency reduced steadily. When i was 4.93~7.39 mA/cm², the concentration of active chlorine increased with the increase of i , but no longer increased when the i exceeded 7.39 mA/cm². The concentration of active chlorine and CE increased with the increase of NaCl concentration, but the increased range reduced. Acidic electrolyte was beneficial to electrogeneration of active chlorine. During the electrolysis, the TSD decreased steadily and the change of pH value did not exceed 1.

Key words: active chlorine; Ti/Pt anode; diluted NaCl solution; electrolysis