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发泡镍电极电化学还原嘌呤中间体

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摘要: 由三维发泡镍电极 H_2SO_4 电解质和阳离子交换膜, 组成隔膜式三维发泡镍电解循环装置. 利用该装置将 3-甲基-4-亚氨基-5-异亚硝基脲 (NAU) 电还原为 3-甲基-4,5-二氨基脲 (DAU). 比较发泡镍阴极的电流密度, 测定不同 pH 条件下的反应电位. 结果表明, 发泡镍电极的电流密度比平板镍高 77.3% ~ 86.7%, 电流效率平均 90.3%, NAU 还原转化率平均 98.4%, 电还原能耗平均 2.92 kWh/kg. 恒电流电还原过程出现峰电位, 继续延长电还原时间则有副反应产生. 分别以传统铁粉还原和电还原的 DAU 完成下游嘌呤产品的合成, 证明电还原产品收率不低于铁粉还原.

关键词: 发泡镍; 三维电极; 电化学还原; 嘌呤

中图分类号: O 646

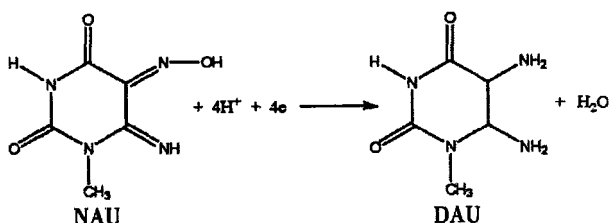
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3-甲基-4-亚氨基-5-异亚硝基脲 (俗称 NAU) 经氢化还原成 3-甲基-4,5-二氨基脲 (DAU), 是合成嘌呤类药物的中间体. NAU 呈玫瑰红色, 分子式为 $\text{C}_5\text{H}_6\text{N}_4\text{O}_3$, $M = 170.13$. DAU 白色, 分子式为 $\text{C}_5\text{H}_8\text{N}_4\text{O}_2$, $M = 156.2$. NAU 的电化学反应如下^[1]:

阳极:



阴极:



1 NAU 电还原装置及实验

1.1 电解槽结构装置

板框式隔膜电解槽结构装置如图 1 所示^[2]. 其中, 阴极为三维发泡镍电极, 它是由 100 mm × 150 mm × 1.5 mm 发泡镍折叠而成的波纹板组成. 阳极是铅平板电极, 面积 100 mm × 150 mm, 厚 1.5 mm. H_2SO_4 电解质, 电解槽的阴极室与阳极室由阳离子交换膜隔开. 阴极与阳极分别构成两个独立的循环

回路. 电化学还原在阴极室完成. 电解槽材质为有机玻璃. 由螺栓将盖板、阴极室、阳极室、隔膜、支架、密封垫、离子交换膜、电极材料紧密串接. 阴极室体积: 200 mm × 100 mm × 20 mm, 阳极室体积: 200 mm × 100 mm × 10 mm.

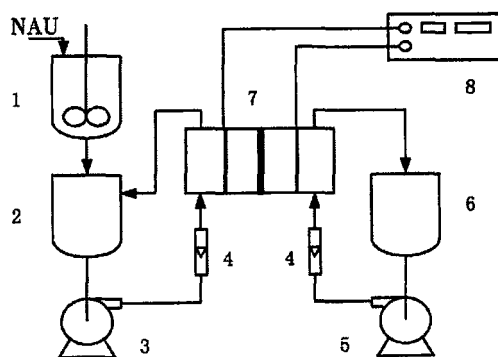


图 1 NAU 电还原实验装置

Fig 1 Experimental device for the NUA Electroreduction

- 1) agitated vessel of catholyte, 2) circulating tank of catholyte, 3) pump of catholyte, 4) flowmeter, 5) pump of anolyte, 6) circulating tank of anolyte, 7) electrolysis cell, 8) direct current power

表 1 发泡镍电极技术指标

Tab 1 Technique parameter of the nickel foam electrode

Nickel content	Pore size	Thickness	Specific weight	Porosity	Resistivity
/ %	/ μm	/ mm	/ $\text{g} \cdot \text{m}^{-2}$	/ %	/ Ωm
> 99	300 ~ 500	1. 5	400	> 95	$< 9 \times 10^{-6}$

表 2 发泡镍电极与平板镍电极电还原 NAU 比较

Tab 2 Comparison between current density of the NAU electroreduction using nickel foam electrode and nickel plate electrode

Voltage of cell	Current of nickel foam	Current density of nickel foam	Current of nickel plate	Current density of nickel plate	Current density relatively
/ V	/ A	/ $\text{A} \cdot \text{m}^{-2}$	/ A	/ $\text{A} \cdot \text{m}^{-2}$	/ %
2. 0	3. 5	233. 3			
3. 0	6. 0	400. 6	0. 8	53. 3	86. 7
3. 5	9. 1	607. 3	1. 3	86. 6	85. 7
5. 0	13. 2	880. 0	3. 0	200. 0	77. 3
8. 0	19. 5	1300. 1	4. 2	280. 0	78. 5

发泡镍是一种新型三维网状多孔金属材料^[3],结构特性见图 2 其特点是,孔隙率高,比表面积大,电阻率低,柔韧性好,乃优良的导电材料.技术指标见表 1.

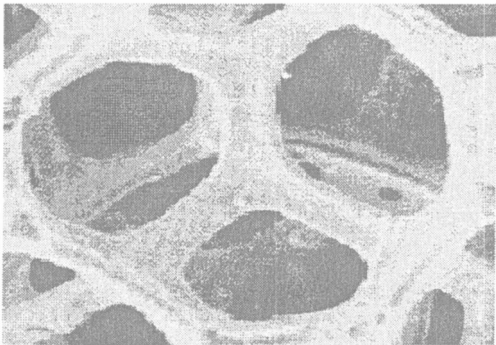


图 2 发泡镍结构
Fig 2 Structural material of the nickel foam

1. 2 电还原实验

电解反应于常温常压下进行.阴、阳极电解质均为 H_2SO_4 溶液.阴极液 NAU 浓度 2%,料液循环体积 500 mL,流量 35 mL/min.实验过程分别以发泡镍和平板镍作阴极材料,测定电解槽的 $V \sim A$ 特性以及电流密度、电解时间、pH 影响、还原转化率等^[3];再以还原后的 DAU 经闭环反应,合成嘌呤产品,并与传统的铁粉还原合成产品比较两者的反应产率.

1. 3 分析方法

由计算机数字模拟采集系统在线分析不同 pH 值、槽电压对还原过程的影响.721 分光光度计(上海第三分析仪器厂),波长 525 nm,检测 NAU 的电流效率.高压液相色谱(日本岛津)检测嘌呤收率.波长 254 nm、C18 柱、流动相 1/3 乙腈、2/3 水.流速 0.5 mL/min.

2 结果与讨论

2. 1 平板镍电极和发泡镍电极电还原 NAU 的 $V \sim A$ 特性比较

平板镍为市售普通镍板.发泡镍购自北京有色金属研究总院.阴、阳极电解质均为 $\text{pH} = 2$ 的 H_2SO_4 溶液.相关实验结果如表 2 所列.由表可见,在相同实验条件下,槽电压为 3 ~ 8 V 时,发泡镍电极的电流密度比平板镍高 77.3% ~ 86.7%.

2. 2 pH 对 NAU 还原过程影响

由计算机数字模拟系统实时监控不同 pH 条件下 NAU 还原电位随时间的变化.阴、阳极电解液体积均为 500 mL,流速 35 mL/min.恒电流还原,电流 2 A.阴极液 NAU 浓度 2%.温度 40℃,检测结果见图 3.实验表明,恒电流条件下,pH 值对还原电位有明显影响,还原电位随酸度增强而下降.当电解液的 pH 为 4 时与 pH 为 8 的相比,相应的还

表 3 NAU的铁粉还原及电还原比较

Tab 3 Comparison between the NAU electroreduction with iron powder reduction

No	Name of Sample	Current efficiency / %	Conversion of NAU / %	Energy Consume of NAU / (kW·h·kg ⁻¹)	Yield Purine / %
1	Reduction of iron powder		96.7		96.2
2	Electroreduction	90	97.5	2.92	98.9
3	Electroreduction	89	98.6	2.94	98.7
4	Electroreduction	92	99.1	2.90	99.4

原电位平均下降幅度为 20% ~ 22%. 还原反应在 2 ~ 40 min 之间有峰电位产生, 且呈现相同的变化规律. 表明该过程物料在电极表面的吸氢反应是逐步完成的. 物料在电极表面的电子转移增加了溶液中的离子浓度而使槽压下降. 当 NAU 完全转化为 DAU 后吸氢饱和, 反应结束. 溶液中的离子浓度恢复至初始值, 还原电位也随之达到起始值. 外观上随着反应的进行 NAU 颜色由玫瑰紫色逐渐变浅, 当还原电位值由峰谷逐渐升至起始电位时, 物料变为无色. 紫外分析同时证明还原过程结束^[4,5].

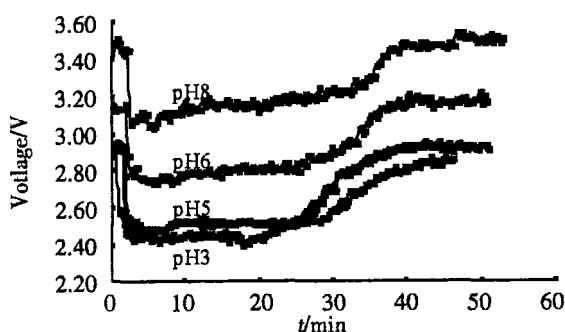


图 3 电还原 NAU 还原电位随溶液 pH 变化关系

Fig 3 Variance of reductive voltage with solution pH for NAU electroreduction

2.3 NAU 电还原效率及嘌呤中间体收率比较

阴极、阳极同前、恒电流 2A 的 H₂SO₄ 电解质、pH 为 2、NAU 浓度 2%. 用分光光度计 525nm 定时检测 DAU 电还原率, 结果见图 4. 如图, 还原过程开始, DAU 随反应时间延长而增加, 到达理论电还原时间时, 电还原转化率达到最大值. 电解时间继续延长, 还原率呈下降趋势. 表明 DAU 还原结束后, 再延长电还原时间将产生副反应.

DAU 在空气中不稳定, 为进一步比较 DAU 还原转化率, 分别用传统的铁粉还原和电还原完成下游产品嘌呤的合成^[6], 高压液相色谱检测. 根据法拉第定律, 当恒电流 A 及相关参数确定后, 电流效率即为理论电还原时间与实际电还原时间之比; 而还原转化率乃为 NAU 反应终止浓度和初始浓度之差与初始浓度之比. 产物分析结果见表 3. 实验结果表明, 电流效率 89% ~ 92%, NAU 还原转化率 97.5% ~ 99.1%, 产品能耗 2.90 ~ 2.94 kW·h/kg.

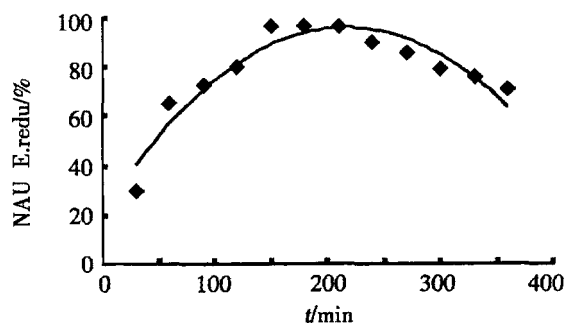


图 4 NAU 转化率随电还原时间变化关系

Fig 4 Variance of the NUA converse with electroreduction time

3 结 论

板框式隔膜电解槽设计结构紧凑, 拆卸方便, 可多级串联用于扩大试验. 高比表面积, 三维发泡镍电极的电流密度比平板镍高 77.3% ~ 86.7%. 其还原电位随电解液 pH 值降低而下降, 就从 pH = 4 与 pH = 8 的相比而言, 前者还原电压平均下降 20% ~ 22%. NAU 还原过程有峰电位产生. 还原结束电位趋于平衡. 该过程为实现自动检测 NAU 还原转化率创造了条件.

发泡镍阴极、铅阳极、阳离子交换膜、板框式

隔膜电解槽电流效率平均 90.3%,NAU 还原转化率平均 98.4%,能耗平均 2.92kW h/kg 经电还原的 DAU 合成之嘌呤产品收率不低于铁粉还原过程.

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Application of Nickel foam Electrode for Electroreduction Intermediate of Purine

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Abstract: Nickel foam with weight uniformity, good porosity, pore size and low resistivity as a three-dimensional cathode was used in a filter-press electrochemical reactor. The H_2SO_4 as supporting electrolyte, separator of cation ion exchange membrane, and the lead plate as an anode were used. The cyclic system consisted of electroreduction reactor, pump, store tank and ampere meter. NAU was electroreduced in the cathode chamber of the reactor. Purine intermediate was synthesized with DAU, and the results were compared with those of iron powder reduction process. A peak current in the electroreduction process was detected. The current density of nickel foam increased by 77.3% ~ 86.7% than that of using plate nickel. The average current efficiency was 90.3% and average conversion of NAU was 98.4%, and average energy consumed was 2.92 kW h/kg, respectively. The Purine yield of electroreduction was similar to that of using iron powder.

Key words: Nickel foam, Three-dimensional electrode, Electroreduction, Filter-press reactor, Intermediate, Purine