

# 贮氢合金用作硝基苯电解加氢 的催化电极研究<sup>①</sup>

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混合稀土贮氢合金是近年来发展起来的新型功能材料, 在室温下它可以吸收比自身体积大几百倍的氢原子形成金属氢化物。这种金属氢化物可作为氢源提供高反应活性的氢原子, 参与有机物的加氢反应; 而合金本身为过渡金属间化合物, 又有良好的催化活性, 同时兼作有机加氢反应催化剂<sup>[1,2]</sup>。在电化学中应用贮氢合金电解水吸收氢形成金属氢化物, 应可作为高效催化电极用于有机物的电化学加氢反应。本工作以硝基苯电解加氢反应为例, 探索这一方法的可行性和反应性质。

## 1 实 验

实验用贮氢合金为富镧混合稀土AB<sub>5</sub>型合金(“迪龙”牌)。贮氢电极为聚四氟乙烯粘接型膜电极(2×3 cm<sup>2</sup>, 约0.9 g)。除特别说明外, 电解前贮氢负极采用恒电流充放电(4~5次)活化以达到稳定的贮氢容量。电解池为H-型玻璃池。阴阳极室采用双层玻璃砂芯分隔。参比电极为饱和甘汞电极。

阴极室电解液分别采用含硝基苯的水溶液和甲醇-水(80:20)溶液, 支持电解质为0.5 mol/L KOH。电解时通Ar气除氧并搅拌溶液。反应过程中溶液组成的变化, 反应产物和中间物的定性定量分析采用紫外光谱(日本岛津UV-3100)和高效液相色谱(日本岛津LC-10A型)分离测定。液相色谱分离柱为SHIM-PACK SBC-ODS。紫外检测波长为290 nm。用硝基苯和苯胺、氧化偶氮苯、偶氮苯等几种可能的产物配成标准样品, 确定保留时间和浓度因子, 以进行定性和定量分析。

在含硝基苯的0.5 mol/L KOH水溶液中, 贮氢合金循环伏安曲线的测定采用粉末微电极法, 微电极的制备参见文献[3]。电解合成采用8511B型恒电位仪(延边龙井产)。

实验药品均为市售分析纯试剂, 使用二次蒸馏水配制溶液。

## 2 结果与讨论

### 2.1 水溶液中硝基苯的催化加氢

为实现有机物的催化加氢, 必须使用特定的催化剂并保持一定的氢压, 常温下贮氢合金内

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氢浓度高,在常压下就可以实现催化加氢.

将电解贮氢后电极置于含硝基苯的饱和水溶液中,采用HPLC跟踪溶液组成的变化,结果如图1所示.很明显,硝基苯在贮氢合金的作用下发生了还原反应.产物主要为苯胺(产率86%),少量的副产物为氧化偶氮苯以及微量偶氮苯.

利用充电曲线法测定反应结束后电极的贮氢容量,发现贮氢电极中的氢原子在反应过程中被消耗,说明电极中溶解氢参与了反应.

硝基苯和苯胺在紫外区的最大特征吸收峰分别为278 nm和230 nm,采用紫外光谱可灵敏地观测硝基苯化学催化加氢过程的组成变化.图2为充电后的贮氢电极放入硝基苯溶液中不同时间测得的UV谱图.可以看到,随着时间延长苯胺的增加和硝基苯的减少,与上述HPLC结果一致.由于在整个反应过程中氧化偶氮苯和偶氮苯的含量很低(图1),说明反应过程中要么主要是硝基苯直接还原为苯胺,要么中间产物苯羟胺进一步加氢还原为苯胺,因速度很快,难于大量积累.

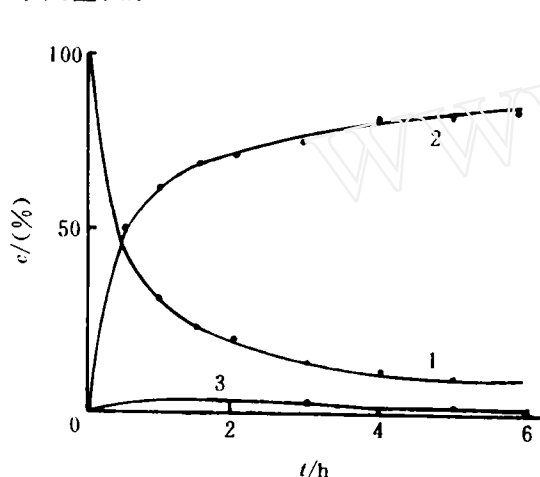


图1 充电后的贮氢电极置于饱和硝基苯水溶液中体系组成随时间的变化

1. 硝基苯, 2. 苯胺, 3. 氧化偶氮苯

Fig. 1 Compositional variation of the system with time for charged hydrogen-storage alloy electrode in 0.5 mol/L KOH solution saturated with nitrobenzene

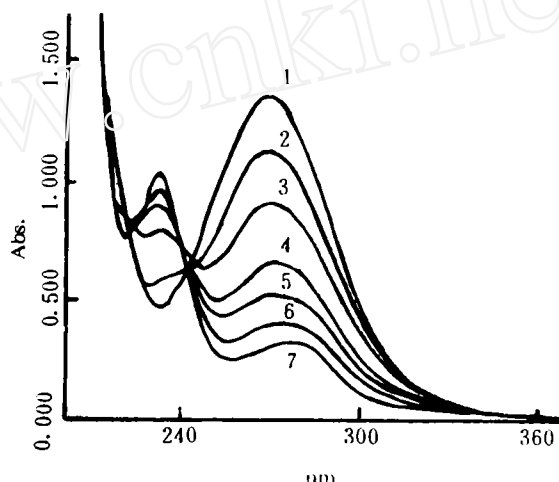


图2 饱和硝基苯水溶液中放入充电活化贮氢合金后溶液的紫外光谱随时间的改变

反应时间h: 1. 0, 2. 1, 3. 2, 4. 3, 5. 4, 6. 5, 7. 6

Fig. 2 UV spectra of the same system as in fig. 1 at different time

通过上述实验结果,可以认为硝基苯在贮氢合金上通过催化加氢高选择性地生成苯胺:



## 2.2 水溶液中硝基苯的电解加氢

图3中曲线1为贮氢合金粉末微电极在0.5 mol/L KOH水溶液中的循环伏安曲线<sup>[3]</sup>. 主要特征为 $E < -0.9$  V处氢的还原峰和 $E = -0.85$  V处氢的氧化峰,前者为电化学吸氢,后者为氢



还原. 当然, 电解过程中水的还原不断产生的氢原子也能参与反应. 因此, 电解硝基苯生成苯胺过程既有催化加氢, 也有电化学加氢, 为一种混合的加氢反应机理.

表1 贮氢电极上硝基苯催化加氢的分析数据

Tab. 1 Experimental data of catalytic hydrogenation of nitrobenzene on MH electrodes

序号	实 验 方 式	介 质	产物产率(%)			转化率(%)	电流效率(%)
			苯胺	氧化偶氮苯	偶氮苯		
1	催化加氢	H <sub>2</sub> O	86	1	1	90	
2	恒电位-1.2 V 电解	H <sub>2</sub> O	86	1.6	0.4	90	>100
3	恒电流 30 mA 电解	H <sub>2</sub> O	88	1.5	0.8	93	92
4	恒电流 30 mA 电解	H <sub>2</sub> O	82	0.25	0.2	83	31
5	恒电流 30 mA 电解	CH <sub>3</sub> OH+H <sub>2</sub> O	86	2	0.7	92	85

同样条件下恒电流电解硝基苯, 反应物和产物组成的变化关系如图5所示. 苯胺的产率为88%, 电流效率为92%. 比较电解前后贮氢电极的容量, 没有检测出明显的变化. 说明贮氢合金在硝基苯的还原过程中没有遭受明显的中毒, 反应活性稳定. 与恒电位电解在电流效率上的区别, 可能是由于电极的极化方式不同造成的. 在恒电流电解时, 溶解氢的消耗由于及时得到了补充, 可以保持较高的反应速度.

以未活化的贮氢合金电极恒电流电解硝基苯, 主要产物同样为苯胺(表1 序号4). 反应过程中溶液组成变化的分析数据与图2类似. 说明反应按加氢还原的方式进行. 此时电流效率较低(31%). 主要是由于未活化的贮氢合金吸氢和贮氢能力差, 大部分氢原子在表面复合成氢分子析出所致.

### 2.3 甲醇-水溶液中硝基苯的电解加氢

由于硝基苯在水溶液中的溶解度低(0.19%, 20℃), 难于进行实际工业应用, 为了探索硝基苯电解加氢在工业生产中的应用的可能性, 我们以甲醇-水混合溶剂为介质进行了同样的研究.

首先将贮氢电极充电活化, 然后恒电流电解含硝基苯的甲醇-水溶液, 反应物和产物在电解过程中的浓度变化与以水为介质类似, 除极少量的氧化偶氮苯和偶氮苯外, 在整个反应过程中未能检测出其它中间产物, 硝基苯的消耗和主要产物苯胺的生成量基本相当, 表明以甲醇-

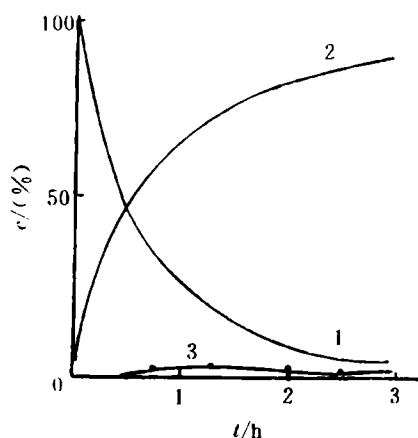


图5 贮氢电极恒电流(30 mA)电解硝基苯时溶液组成随时间的变化关系

1. 硝基苯, 2. 苯胺, 3. 氧化偶氮苯

Fig. 5 Compositional variation of the system of hydrogen-storage alloy electrode in 0.5 mol/L KOH solution saturated with nitrobenzene with time

水为介质电解硝基苯的过程与以水为介质类似,其加氢反应机理可用式(2)描述.

由表1(序号5)可知,恒电流电解硝基苯生成苯胺的产率为86%,电流效率85%,接近于以水为介质(表1序号3)时的数据.说明贮氢合金电极在甲醇-水溶液中对硝基苯加氢反应同样表现为良好的催化活性.与以水为介质类似,电解前后电极贮氢容量基本不变.在反应体系中大量甲醇的存在不会造成电极的中毒.

### 3 结 论

通过以上研究,可以认为:

1)贮氢合金作为催化电极用于硝基苯加氢还原,有催化反应活性高,对产物苯胺选择性强(产率达88%),电流效率高(90%)等显著优点,同时价格相对低廉,可以替代贵金属催化剂,用于化学加氢或电解有机物加氢反应.

2)以甲醇-水为介质电解硝基苯,发现采用贮氢合金作为催化电极时,对苯胺生成的选择性强(产率86%),电流效率高(85%),催化活性稳定.这一体系具有良好的工业化应用前景.

## A Investigation of Hydrogen-storage Alloy as Catalytic Electrode for Hydrogenation of Nitrobenzene

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**Abstract** Since hydrogen-storage alloy can not only absorb hydrogen atoms to form highly reactive metal hydride as hydrogen source by electrolysis but also possesses a certain catalytic activity for hydrogenation, it is thus feasible to utilize the alloy as a novel electrode for electrolytic hydrogenation in organic electroreduction. This work employed misch metal  $AB_5$  type alloy as a catalytic electrode and studied the electrochemical hydrogenation of nitrobenzene.

The hydrogen-storage electrode (MH) was a plastic bonded electrode sheet made from a paste of Mm ( $NiCoMnAl$ )<sub>5</sub> alloy powder and teflon emulsion. The electrolysis was performed at constant current and controlled potential in a three electrode cell of H-type configuration. The electrolyte was 0.5 mol/L KOH aqueous solution and 0.5 mol/L KOH in  $CH_3OH + H_2O$  (80 : 20 by vol.). Changes in the concentrations of nitrobenzene (NB) and its reaction products were monitored by sampling at different duration of electrolysis and then analysed by HPLC and UV spectroscopy.

The CV curve of a powder microelectrode of hydrogen-storage alloy in alkaline solution showed a pair of distinct oxidation-reduction current peaks of hydride formation at  $E = -1.1$  V and hydrogen desorption at  $E = -0.9$  V. In addition of NB, a strong reduction peak appeared at  $E = -0.7$  V on

cathodic scan, and the anodic peak of hydride oxidation completely disappeared on reverse scan to suggest the participation of absorbed hydrogen in the NB reduction (Fig. 3). In the electrolysis of NB-saturated alkaline solution, we used UV spectroscopy monitoring the compositional changes of the electrolyte. It was found that with increasing the electrolysis time the concentration of NB dropped steadily and instead the concentration of the main product aniline (AN) went up continuously as seen by the decreasing 278 nm and increasing 230 nm UV peaks both characteristic of nitrobenzene and aniline. By HPLC separation and analysis of the electrolyte after electrolysis, the electrolysis yield of AN reached up to 90% and the current efficiency calculated also exceeded 85%. Except for a very small amount of azoxybenzene and azobenzene (totally about 2% content) there were no any other side reaction products or intermediates found in the course of electrolysis, indicating the high selectivity of MH electrode for nitrobenzene hydrogenation.

In order to increase the dissolubility of NB in electrolyte, we tried to use the methanol-water mixed solvent instead of aqueous solvent for the electrolytic hydrogenation of NB. In the case of using the mixed solvent, the main electrolysis product was still AN, and the AN yield and current efficiency were 86% and 85% both almost equal to the values measured in alkaline solution. Comparing of the MH electrodes before and after electrolysis there were no any discernible changes observed in the hydrogen-storage capacity and charge-discharge properties, suggesting a quite catalytic stability in the organic media.

In summary it could be concluded that the use of MH electrode in the electrochemical hydrogenation of nitrobenzene offers a number of advantages of high selectivity, high current efficiency and excellent catalytic stability, this shows a great promise for industrial applications.

**Key words** Hydrogen-storage alloy, Electrocatalysis, Hydrogenation, Nitrobenzene

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