

碱性溶液中锌电极缓蚀的研究

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摘要: 用线性电位扫描、交流阻抗和实体电池放电实验研究了硝酸铅($\text{Pb}(\text{NO}_3)_2$)和十二烷基苯磺酸钠(SDBS)及二者组成的复合添加剂对在 $3 \text{ mol} \cdot \text{L}^{-1}$ KOH 溶液中锌电极电化学行为的影响。结果表明:两种添加剂均具有一定的缓蚀作用,而其复合添加剂的协同效应、缓蚀效果最佳。

关键词: 添加剂; 锌; 缓蚀; 电化学行为

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锌广泛用作碱性电池的负极活性材料^[1-6],但容易被腐蚀,其腐蚀过程是阳极溶解和阴极析氢。锌的自放电导致电池漏液、容量下降、使用寿命缩短等问题^[1-2]。以往大多使用汞、铅、镉、铬酸盐、亚硝酸盐等添加剂以遏制锌电极的腐蚀,但均有毒,且效果也不尽人意,而使用钢、镓及其氧化物、氢氧化物或其他有机添加剂又因价格昂贵备受限制。本文研究了由硝酸铅及十二烷基苯磺酸钠组成的复合添加剂对锌电极在 KOH 溶液中的电化学特性的影响。

1 实验

1.1 电化学方法

三电极体系:研究电极为锌棒($\phi 3.18 \text{ mm}$),经环氧树脂固封,依次用 800#、2000#、2400#和 4000#砂纸打磨、丙酮超声清洗、二次蒸馏水冲洗;对电极为铂片;参比电极 Hg/HgO。电解液为 $3 \text{ mol} \cdot \text{L}^{-1}$ KOH。使用 PGSTAT-30(Auto-lab, Eco·Echemie B. V. Co. 荷兰),实验之前锌电极先于 -1.5 V 极化 30 min 后测试。

1.2 电池和仪器

组装 AG13 碱性锌锰扣式电池,以复合添加剂替代原汞、钢添加剂,1 mA 放电,由 LAND 电池测

试系统(Land CT 2001A)采集数据。

使用 JSM-6380LV(JEOL, 日本)扫描电子显微镜(SEM)观察锌形貌,加速电压 10~30 kV。

2 结果与讨论

2.1 阴极极化

图 1 示出锌电极在含不同添加剂碱溶液中的阴极极化曲线。可以看出,无添加剂时锌电极析氢严重。加入 SDBS 后,析氢反应仅被少许抑制。但 $\text{Pb}(\text{NO}_3)_2$ 则可对锌电极的析氢反应起到很好的抑制作用。如果用复合添加剂,那么锌表面的析氢反应立即受到极大抑制,这就是双组分添加剂所产生的协同效应。

2.2 阳极极化

锌电极在含有不同添加剂的碱溶液中的阳极极化曲线如图 2 所示。可以看出, $\text{Pb}(\text{NO}_3)_2$ (曲线 c)使锌电极溶解延后,该曲线第 1 阳极峰电位正移 50 mV,而第 2 个阳极峰电流稍有增加,表明铅可较强地抑制锌的初期溶解,对锌电极的深度放电有所促进;就 SDBS(曲线 b)而言,锌电极起波电流提前;而复合添加剂阳极极化(曲线 d)与 SDBS 的相似,不过对应的电流稍小,表明该复合添加剂对锌电极的阳极溶解也有一定的抑制作用,但基

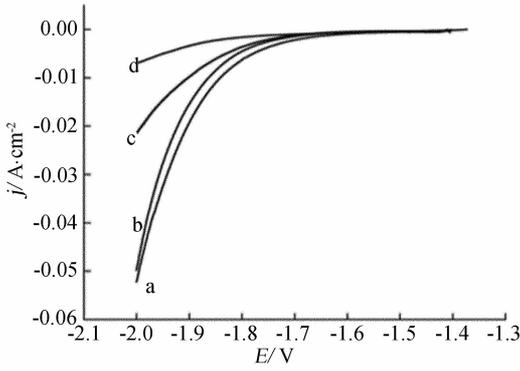


图 1 锌电极在含不同添加剂的 $3 \text{ mol} \cdot \text{L}^{-1}$ KOH 溶液中阴极极化曲线

Fig. 1 Cathodic polarization curves of the zinc electrode in $3 \text{ mol} \cdot \text{L}^{-1}$ KOH solution containing different additives (scan rate: 20 mV/s)

a. no additives; b. 500 mg/L SDBS; c. 10 mg/L $\text{Pb}(\text{NO}_3)_2$; d. 500 mg/L SDBS + 10 mg/L $\text{Pb}(\text{NO}_3)_2$

2.3 线性电位扫描

图 3 示出锌电极在含有不同添加剂的碱溶液中的极化曲线. 如图, SDBS 添加剂(曲线 b)使锌电极腐蚀电位稍负移, 其表面阴极析氢受抑制的程度较小, 阳极呈现一定程度的活化; $\text{Pb}(\text{NO}_3)_2$ (曲线 c) 和复合添加剂(曲线 d) 均使该电极腐蚀电位正移, 阴阳极电流有所减小, 而阴极电流下降甚多, 说明该添加剂主要抑制阴极过程, 虽然其阳极起始电流小于无添加剂的, 但随着电位正移至 -1.35 V , 二者电流趋于同值, 表明前者并不影响该电极后期的放电行为.

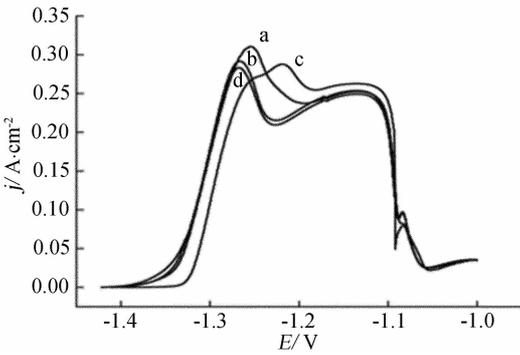


图 2 锌电极在含不同添加剂的 $3 \text{ mol} \cdot \text{L}^{-1}$ KOH 溶液中阳极极化曲线

Fig. 2 Anodic polarization curves of the zinc electrode in $3 \text{ mol} \cdot \text{L}^{-1}$ KOH solutions containing different additives (scan rate: 20 mV/s)

a. no additives; b. 500 mg/L SDBS; c. 10 mg/L $\text{Pb}(\text{NO}_3)_2$; d. 500 mg/L SDBS + 10 mg/L $\text{Pb}(\text{NO}_3)_2$

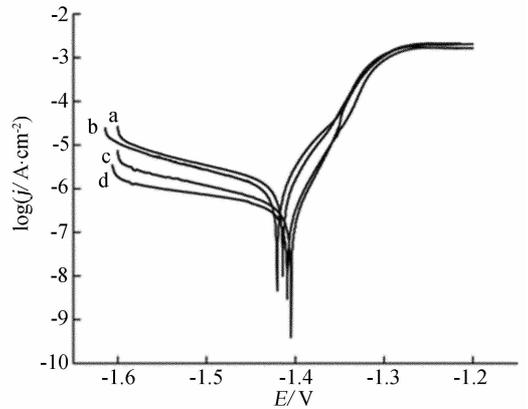


图 3 锌电极在含不同添加剂 $3 \text{ mol} \cdot \text{L}^{-1}$ KOH 溶液中极化曲线

Fig. 3 Effects of different additives on the polarization curves of zinc electrode in $3 \text{ mol} \cdot \text{L}^{-1}$ KOH solution (scan rate: 1 mV/s)

a. no additives; b. 500 mg/L SDBS; c. 10 mg/L $\text{Pb}(\text{NO}_3)_2$; d. 500 mg/L SDBS + 10 mg/L $\text{Pb}(\text{NO}_3)_2$

缓蚀效率^[7] 计算如下:

$$\eta = (I_{\text{corr}} - I_{\text{corr}}') / I_{\text{corr}} \quad (1)$$

本不影响锌电极的活化溶解.

表 1 锌电极在含不同添加剂的 $3 \text{ mol} \cdot \text{L}^{-1}$ KOH 溶液中的腐蚀电化学参数

Tab. 1 Electrochemical corrosion parameters of the zinc electrode in $3 \text{ mol} \cdot \text{L}^{-1}$ KOH solutions containing different additives

Additive	E_{corr}/V	$I_{\text{corr}}/\text{A} \cdot \text{cm}^{-2}$	$\eta/\%$
Blank	-1.414	2.07×10^{-4}	
500 mg/L SDBS	-1.420	1.60×10^{-4}	22.7
10 mg/L $\text{Pb}(\text{NO}_3)_2$	-1.404	6.39×10^{-5}	69.1
500 mg/L SDBS + 10 mg/L $\text{Pb}(\text{NO}_3)_2$	-1.409	4.22×10^{-5}	79.7

式中 I_{corr} 、 I'_{corr} 为添加剂加入前后锌的腐蚀电流. 所得相关电化学参数列于表 1. 如表可知, 各种添加剂均使锌的腐蚀电流减小, 其中复合添加剂缓蚀效果最佳.

2.4 电极交流阻抗

图 4 是锌电极在含有不同添加剂碱溶液中的交流阻抗谱图, 频率范围 $10^{-2} \sim 10^5$ Hz. 谱图中, 高频部分的半圆直径表示电化学反应电阻^[8]. 依下式可得该电极缓蚀效率^[9]:

$$\eta = (R_{reac} - R'_{reac}) / R_{reac} \quad (2)$$

式中 R'_{reac} 、 R_{reac} 分别表示添加剂加入前后锌电极电化学反应电阻, 表 2 列出相关计算结果. 由表可见, 在含有添加剂的电解液中, 锌电极电化学反应电阻增大, 锌腐蚀减缓. 其中以复合添加剂的抑制程度最高, 缓蚀效率达 81.1%.

表 2 锌电极在含不同添加剂碱溶液中开路电位的电化学反应电阻及缓蚀剂的缓蚀效率

Tab. 2 Reaction resistance and corrosion inhibition efficiency for zinc electrode in $3 \text{ mol} \cdot \text{L}^{-1}$ KOH solutions containing different additives at open circuit potential

Additive	R_{reac} / Ω	$\eta / \%$
Blank	60	
500 mg/L SDBS	77	22.1
10 mg/L $\text{Pb}(\text{NO}_3)_2$	189	68.3
10 mg/L $\text{Pb}(\text{NO}_3)_2 + 500 \text{ mg/L SDBS}$	316	81.1

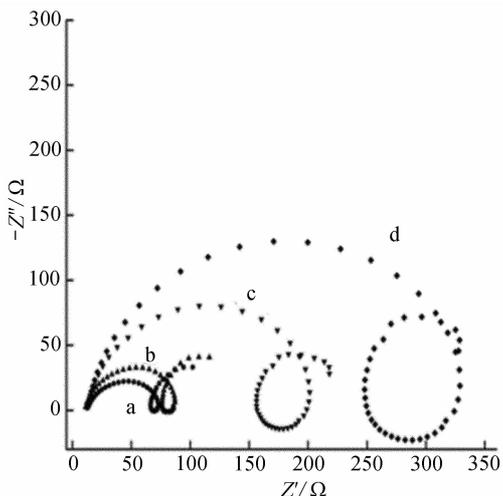


图 4 锌电极在含不同添加剂的 $3 \text{ mol} \cdot \text{L}^{-1}$ KOH 溶液中开路电位交流阻抗图谱

Fig. 4 Nyquist plots of the zinc electrode in $3 \text{ mol} \cdot \text{L}^{-1}$ KOH solutions containing different additives at open circuit potential a. no additives; b. 500 mg/L SDBS; c. 10 mg/L $\text{Pb}(\text{NO}_3)_2$; d. 500 mg/L SDBS + 10 mg/L $\text{Pb}(\text{NO}_3)_2$

2.5 扫描电镜

图 5 是锌在不同添加剂碱溶液中搁置 5 d 的扫描电镜照片. 可以看出, 电解质无添加剂时 (a), 锌表面凹凸不平, 存在多又深的蚀孔, 腐蚀严重. 缓蚀剂加入后, 锌受蚀程度因添加剂不同而异 (b ~ d), 锌表面出现的蚀孔少又浅, $\text{Pb}(\text{NO}_3)_2$ 较 SDBS 添加剂的缓蚀效果更好. 对比之下复合添加

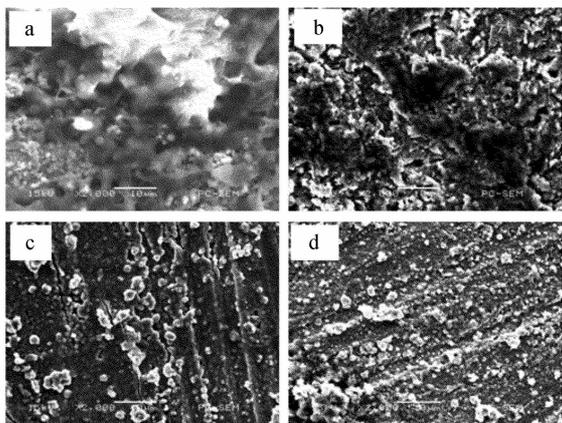


图 5 锌在含不同添加剂的 $3 \text{ mol} \cdot \text{L}^{-1}$ KOH 中搁置 5 d 扫描电镜照片 (放大 2000 倍)

Fig. 5 SEM images of the zinc electrode in $3 \text{ mol} \cdot \text{L}^{-1}$ KOH solutions containing different additives for 5 days (2000 ×) a. blank; b. 500 mg/L SDBS; c. 10 mg/L $\text{Pb}(\text{NO}_3)_2$; d. 500 mg/L SDBS + 10 mg/L $\text{Pb}(\text{NO}_3)_2$

剂缓蚀效果最佳, 锌表面相对平整, 无蚀孔.

2.6 电池放电性能

图 6 示出由作者组装的 AG13 扣式碱性锌锰电池 (45°C 烘烤 10 h) 1 mA 的恒流放电曲线. 可以看出, 含上述复合添加剂电池的放电容量 (曲线 b) 较市售电池 (曲线 a) 大 14 mAh, 增加了 11.7%.

2.7 缓蚀机理探讨

SDBS + $\text{Pb}(\text{NO}_3)_2$ 添加剂有最好的缓蚀性能, 这可能是由于 SDBS 具有链状结构和环状结构, 且 $\text{Pb}(\text{NO}_3)_2$ 可置换 Zn 而覆盖于表面, 而 Pb 含有 p 空轨道, 能接纳 SDBS 硫的孤对电子而吸附于电极表面, Pb 的析氢高过电位和 SDBS 较好的阻隔功

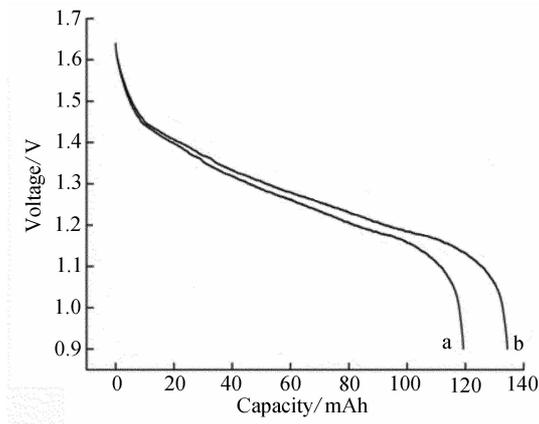


图6 AG13 扣式碱性锌锰电池 1 mA 放电曲线

Fig. 6 The continuous discharge curves (at 1 mA) for AG 13 button alkaline manganese dioxide/zinc batteries commercial (a), 500 mg/L SDBS + 10 mg/L Pb (NO₃)₂(b) were used as the additives

能起协同效应,从而大大降低锌的腐蚀.

3 结论

500 mg/L SDBS 和 10 mg/L Pb(NO₃)₂ 复合添加剂对碱溶液中锌电极的缓蚀效率最佳,高达 80%,这可能是来自 Pb 的析氢高过电位和 SDBS 较好阻隔功能的协同效应.

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Effects of Additives on the Electrochemical Behaviors of Zn Electrode in Alkaline Solutions

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Abstract: Electrochemical behaviors of Zn electrode in $3 \text{ mol} \cdot \text{L}^{-1}$ KOH solution containing the single additive ($\text{Pb}(\text{NO}_3)_2$, SDBS) and the mixed additives ($\text{Pb}(\text{NO}_3)_2 + \text{SDBS}$) were investigated. The results were showed that the additives could suppress the corrosion of zinc in $3 \text{ mol} \cdot \text{L}^{-1}$ KOH solution. And the inhibition efficiency of the mixed additives was higher than that of any single additive.

Key words: additives; zinc; inhibition; electrochemical behavior