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聚天冬氨酸和钨酸钠复配对 3% NaCl 溶液中白铜 B10 的缓蚀作用

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摘要: 应用交流阻抗法和极化曲线法, 研究了两种环境友好型水处理药剂, 即聚天冬氨酸 (PASP) 和钨酸钠的单一配方及其复配对白铜 (B10) 在 3% NaCl 溶液中的缓蚀效果。研究表明: 单一聚天冬氨酸或钨酸钠配方对 B10 均具有一定的缓蚀效果, 其中聚天冬氨酸以浓度为 40 mg/L, 钨酸钠以浓度为 60 mg/L 时的缓蚀效果最佳。总浓度为 40 mg/L 的两者复配具有更加明显的缓蚀效果并显示出协同效应, 其中以聚天冬氨酸与钨酸钠配比为 3:1 的缓蚀效果最佳。

关键词: 聚天冬氨酸; 钨酸钠; 白铜 B10; 缓蚀剂; 交流阻抗

中图分类号: TG 174

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研发金属缓蚀剂是以高效绿色环保为主要目标。钨酸盐因其毒性低, 对环境、人体和作物几乎没有危害, 也不引起微生物滋生, 属环境友好型缓蚀剂, 已引起人们的广泛兴趣^[1-6]。但单一使用钨酸盐其缓蚀效率还不够高, 而且用量较大, 对此可利用不同缓蚀剂之复配来提高缓蚀效率。聚天冬氨酸 (PASP) 是新近发现的一种绿色水处理药剂^[7-8], 具有优异的阻垢分散性能和良好的可生物降解性, 以其作为阻垢剂方面的研究与应用已受到各方面的重视, 但有关它的缓蚀性能研究还不多^[9], 特别是用于白铜 (B10) 缓蚀剂的研究国内外还未见报道。本文试将钨酸钠和聚天冬氨酸这两种环境友好型水处理药剂相结合, 初步研究其单一及复合的配方对白铜 (B10) 在 3% NaCl 溶液中的缓蚀作用, 并优化其最佳的缓蚀剂配方。

1 实验

交流阻抗和极化曲线测试: PAPC M283 恒电位仪, PARC 1025 频谱分析仪, 配套软件为 PARC M398, PARC M352, 阻抗测试频率范围 0.05 Hz ~

100 kHz, 激励信号峰值 5 mV, 极化曲线测试扫描速率 1 mV/s

电极制备: B10 电极用环氧树脂密封, 面积 1 cm², 测量前电极表面经金相砂纸逐级打磨抛光, 无水乙醇除油, 去离子水冲洗干净后放入电解池。三电极体系, 工作电极为 B10 电极; 铂电极作辅助电极; 参比电极是双液接饱和甘汞电极。

试剂: 实验药品均为分析纯, 溶液用去离子水配制。

交流阻抗和极化曲线实验均是先将 B10 电极浸入含一定浓度缓蚀剂的 3% NaCl 溶液中, 经浸泡 1 h 后再于开路电位下测其阻抗谱图或在给定电位范围内测定极化曲线。

2 结果与讨论

2.1 单一 PASP 和 Na₂WO₄ 对 B10 的缓蚀效果

图 1 为 B10 电极分别浸入含有不同浓度 PASP 的 3% NaCl 溶液中经 1 h 后测得的 Bode 图谱。鉴于该体系的阻抗谱图均属同一类型, 故可根据低频

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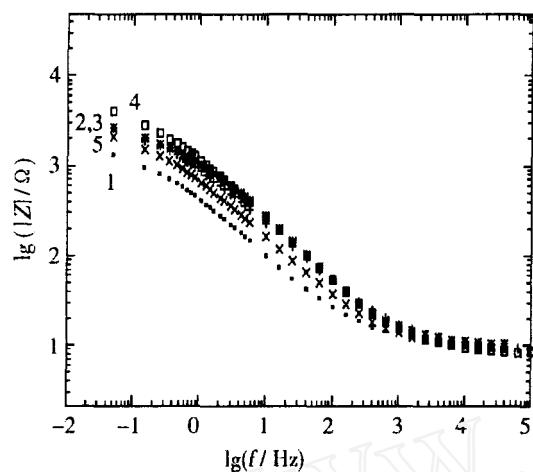


图 1 B10 电极分别浸入含有不同浓度 Pasp 的 3% NaCl 溶液中经 1 h 后的 Bode 图

Fig 1 Bode plots of the B10 electrodes immersed in 3% NaCl solution with different concentrations of Pasp
Pasp concentration/ $\text{mg} \cdot \text{L}^{-1}$: 1) Blank, 2) 20,
3) 50, 4) 40, 5) 60

阻抗值的高低来判断缓蚀剂性能,即阻抗值越大说明其对金属的缓蚀效果越好^[10]. 图 1 示出其于低频处显示的阻抗因 Pasp 浓度的变化而不同,而且含有不同浓度 Pasp 的各曲线阻抗均比未添加 Pasp(曲线 1)的阻抗高,可见 Pasp 的存在对 B10 起到了一定的缓蚀作用,或者说 B10 的耐蚀性能增加;增加 Pasp 的浓度至 40 mg/L 时,其对应的阻抗值也明显上升并达到最大,说明此时缓蚀效果最好,B10 表现出来的耐蚀性能最佳;继续增加 Pasp 浓度至 50 或 60 mg/L,阻抗值反而有所下降,即 B10 耐蚀性能降低,这可能是缓蚀剂的浓度极值现象^[11]所引起的.

图 2 为 B10 电极分别浸入含有不同浓度钨酸钠的 3% NaCl 溶液中经 1h 后测得的 Bode 图谱. 如图可见,各曲线的变化规律与图 1 均相似,当 Na_2WO_4 的浓度增至 60 mg/L 时,对应的阻抗值明显增大,表明此时的缓蚀效果,从而也是 B10 的耐蚀性能较好.

2.2 Pasp 和钨酸钠复配对 B10 的缓蚀效果

以上表明,虽然与不添加缓蚀剂的空白试验相比,单一聚天冬氨酸或单一钨酸钠对 B10 的缓蚀性能均有提高,但效果还不臻理想.为此本文尝试以 Pasp 与 Na_2WO_4 复配 B10 缓蚀剂,并参照浓度

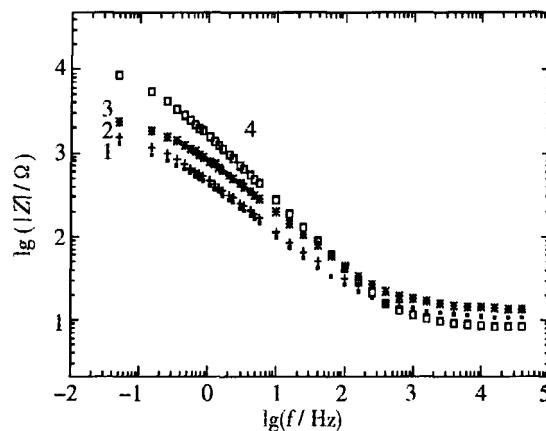


图 2 B10 电极分别浸入含有不同浓度 Na_2WO_4 的 3% NaCl 溶液中经 1 h 后测定的 Bode 图谱

Fig 2 Bode plots of the B10 electrodes immersed in 3% NaCl solution after 1 h with different concentrations of Na_2WO_4
 Na_2WO_4 concentration/ $\text{mg} \cdot \text{L}^{-1}$: 1) Blank, 2) 20,
3) 40, 4) 60

为 40 mg/L 的单一 Pasp 缓蚀效果最好,选择两者总浓度为 40 mg/L 按不同比例进行复配,结果发现,当 [Pasp] / [Na₂WO₄] 以 3 : 1 复配时缓蚀效果最佳. 图 3 示出,由复配得到的阻抗值比空白及单一配方的都有明显增加,约大 2 个数量级,可见复配对 B10 缓蚀作用显著而且具有缓蚀协同效应.

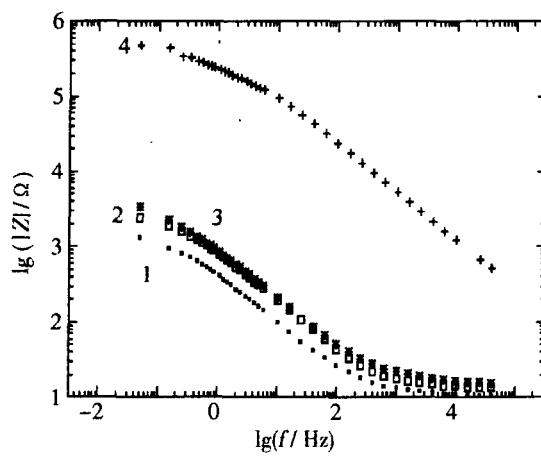


图 3 B10 电极浸入在含不同缓蚀剂的 3% NaCl 中经 1 h 后的 Bode 图

Fig 3 Bode plots of the B10 electrodes immersed in 3% NaCl solution after 1 h with various inhibitors
1) Blank, 2) 40 mg/L Na_2WO_4 ,
3) 40 mg/L Pasp,
4) 30 mg/L Pasp + 10 mg/L Na_2WO_4

2.3 极化曲线法对B10缓蚀性能的研究

图4给出白铜(B10)电极在含有不同缓蚀剂的3%NaCl溶液中经浸泡1 h后测得的极化曲线。表1列出各试验体系的腐蚀电位和腐蚀电流密度。如表,与空白试验比较,尽管白铜(B10)在3%NaCl溶液中的腐蚀电流于加入40 mg/L的 Na_2WO_4 或40 mg/LPASP后均有不同程度的降低,但比起由30 mg/LPASP+10 mg/L Na_2WO_4 复配的缓蚀剂,后者的腐蚀电流更是大幅度明显降低(仅为0.08 $\mu\text{A}/\text{cm}^2$),可见复配对3%NaCl溶液中的白铜(B10)具有明显的缓蚀效果,而且表现出缓蚀协同效应。这一结果和应用交流阻抗法得出的结论相一致。另从图4极化曲线也可看出,聚天冬氨酸及钨酸钠复配后其阴极极化和阳极极化均受到抑

制,说明复配缓蚀剂对B10的作用机理是混合型缓蚀剂。其中,钨酸钠为阴极型缓蚀剂,聚天冬氨酸为阳极型缓蚀剂。

4 结论

1)单一聚冬天氨酸和单一钨酸钠对白铜(B10)均具有一定的缓蚀效果,其中聚冬天氨酸在浓度为40 mg/L时,钨酸钠在浓度为60 mg/L时缓蚀效果最佳。

2)将聚冬天氨酸与钨酸钠以3:1复配,总浓度为40 mg/L时,对B10表现出明显的缓蚀效果且具有缓蚀协同效应。

3)聚冬天氨酸与钨酸钠复配对B10的缓蚀显示为混合型缓蚀剂。

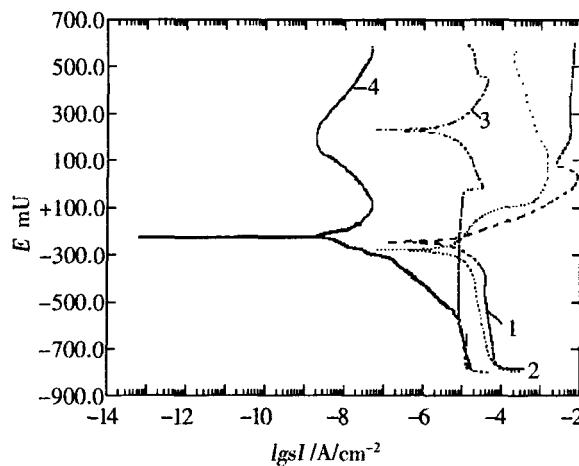


图4 B10电极浸入在含不同缓蚀剂的3%NaCl中经1 h后的极化曲线

Fig 4 Potentiodynamic polarization curves of the B10 electrodes immersed in 3% NaCl solution after 1 h with various inhibitors 1) blank, 2) 40 mg/L Na_2WO_4 , 3) 40 mg/L PASP, 4) 30 mg/L PASP + 10 mg/L Na_2WO_4

表1 白铜(B10)在含不同缓蚀剂的3%NaCl中浸泡1 h后的腐蚀电位和腐蚀电流

Tab 1 Electrochemical parameters of the B10 electrodes immersed in 3% NaCl solution after 1 h with various inhibitors

inhibitors	E_{corr} /mV	I_{corr} / $\mu\text{A} \cdot \text{cm}^{-2}$
B lank	-239.8	24.7
[Na_2WO_4] = 40 mg/L	-291.8	15.1
[PASP] = 40 mg/L	273.4	0.8
30 mg/LPASP + 10 mg/L Na_2WO_4	-213.6	0.1

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The Complex of PASP and Tungstate as Inhibitors of Cupronickel B10's Corrosion in 3% NaCl Solution

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Abstract: AC impedance and polarization curve measurements were conducted to study the effects of environment-friendly inhibitors PASP, Na₂WO₄ and their complexes on the corrosion of cupronickel B10 in 3% NaCl solution. The results indicate that PASP or Na₂WO₄ alone does not inhibit the corrosion of B10, and most effective concentrations are 40 mg/L and 60 mg/L for PASP and Na₂WO₄, respectively. With the total concentration of 40 mg/L for the complex inhibitors, the optimum complex ratio of PASP to Na₂WO₄ was 3:1. The complex of such a combination showed a significantly synergistic inhibition effect on the corrosion of B10.

Keywords: PASP, Sodium tungstate, B10, Inhibitor, AC impedance