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## Structure and Property of Molecular Self-assembled Membrane with Zirconium Ion

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# 锆离子改善十烷基磷酸组装膜结构及性能研究

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**摘要:** 利用烷基磷酸、金属锆离子和不锈钢电极表面的相互作用, 通过表面自组装, 在 304 不锈钢电极表面分别修饰了单层和双层烷基磷酸自组装膜, 采用接触角和极化曲线对修饰电极进行测量. 实验表明, 双层烷基磷酸修饰膜具有更佳的耐腐蚀性能.

**关键词:** 自组装膜; 十烷基磷酸钠; 接触角; 极化曲线; 缓蚀剂

**中图分类号:** O646

**文献标识码:** A

不锈钢具有优良的耐腐蚀性和光泽度而受到广泛应用. 由于不同成分的不锈钢, 其组织形态及在特定环境下的使用, 而可能发生应力腐蚀、晶间腐蚀、点腐蚀等<sup>[1-4]</sup>, 化学钝化和缓蚀剂是现时常用的化学防腐<sup>[5-8]</sup>方法. 化学钝化, 是在一定浓度的酸、给定温度和时间, 使不锈钢生成的钝化膜与溶解达到平衡, 并最终形成一层致密的钝化膜, 从而提高不锈钢的防腐能力的方法<sup>[9]</sup>. 但钝化工艺存在环保问题, 还可能改变器材的精确尺寸及形状. 缓蚀剂可在不锈钢表面吸附, 虽然能在不改变器材尺寸及形状的条件下提高抗腐蚀性能, 但高效缓蚀剂往往具有毒性, 使其应用受到限制. 又由于缓蚀剂浓度较低, 外界环境的微小变化就会对体系造成较大的影响, 制约了缓蚀剂的进一步发展<sup>[10-11]</sup>.

有机磷酸酯可以通过分子自组装技术在金属表面形成单分子膜, 从而降低金属腐蚀速率, 因而可作为金属的缓蚀剂<sup>[12-13]</sup>. Apama Raman 等通过漫反射傅里叶红外光谱确认有机磷酸在不锈钢表面所形成的自组装单分子膜是通过磷酸分子上的两个氧与不锈钢表面的氧化层以“双齿模式”成键<sup>[14]</sup>. 此外, Hubert Mutin 等根据烷基磷酸能与金属锆( $Zr^{4+}$ )离子和金属氧化物发生配位作用, 构筑了自组装有机-无机杂化材料<sup>[15]</sup>.

本文通过层层组装的方法, 尝试在不锈钢表面

构筑烷基磷酸双层吸附自组装膜, 并探讨了锆离子对烷基磷酸自组装膜结构的影响.

## 1 实验部分

### 1.1 自组装膜修饰电极的制备

以 304 不锈钢板 (宝钢集团不锈钢分公司, 成分除 Fe 外,  $C \leq 0.07$ ,  $Cr = 17 \sim 19$ ,  $S \leq 0.01$ ,  $Mn \leq 2$ ,  $P \leq 0.035$ ,  $S \leq 0.03$ ,  $Ni = 8 \sim 11$ , by mass%) 作基底电极, 面积  $0.2 \text{ cm}^2$ . 先经 600# 砂纸上打磨, 再依次用  $0.5$ 、 $0.03 \mu\text{m}$  的氧化铝粉抛光至镜面, 依序用无水乙醇、超纯水冲洗干净. 将电极置于 3% (by mass 下同) NaCl 溶液中、在  $-0.9 \text{ V}$  恒电位下还原 ( $10 \text{ min}$ ), 以去除打磨过程中可能生成的氧化层. 然后将该电极置于  $1 \text{ mmol/L}$  十烷基磷酸钠 (水-乙醇) 溶液中组装一定时间, 制得单层十烷基磷酸钠修饰的不锈钢电极, 记作 MonolayerSS. 金属锆离子能与烷基磷酸发生配位, 因此将十烷基磷酸钠修饰的不锈钢电极 (MonolayerSS) 置于  $1 \text{ mmol/L}$  硝酸锆溶液中浸渍 4 h 后, 取出再用  $N_2$  气吹干, 将此引入锆离子的单分子烷基磷酸修饰电极 (Zr-MonolayerSS), 又置于  $1 \text{ mmol/L}$  十烷基磷酸钠溶液中组装 4 h 即得十烷基磷酸钠双层膜修饰电极, 记作 DoublelayerSS.

### 1.2 接触角

参照 Bain<sup>[16]</sup>方法,用微量取样器移取 1 $\mu$ L超纯水小心滴在裸不锈钢电极或上述制备的各自组装膜修饰电极表面,用 JJC-1 润湿角测量仪(长春第五光学仪器有限公司)测定电极的接触角.并于不同位置的电极表面重复测定 3 次以上,取其平均值.

### 1.3 极化曲线

使用 CH1750 电化学工作站(上海辰华).三电极体系,研究电极为裸不锈钢电极和上述自组装膜修饰的不锈钢电极,参比电极为饱和甘汞电极(SCE),辅助电极为铂片.3% NaCl 为电解液,室温下测试.实验时以开路电位为起始电位,以 10 mV/s 扫描速率分别作阳极和阴极电位扫描.

## 2 结果与讨论

### 2.1 MonolayerSS 修饰电极的性能测试

烷基磷酸分子在不锈钢表面的特性吸附,一般认为是通过磷酸分子中的氧与不锈钢表面原子成键<sup>[15, 17-21]</sup>.十烷基磷酸钠分子同时含有亲水性的磷酸基和疏水性的十烷基长链,当它在不锈钢表面吸附组装时,亲水性的磷酸基朝不锈钢电极表面,而疏水性的烷基链则向溶液,从而增加了不锈钢电极表面的疏水性.表 1 列出裸不锈钢电极及其在十烷基磷酸钠溶液中修饰不同时间获得的电极表面的接触角.实验显示,未经修饰的 304 不锈钢的接触角为 47 $^\circ$ 左右,而经过十烷基磷酸钠修饰的电极接触角明显增大,如组装 4h 的电极其接触角竟达到 106 $^\circ$ 左右.此结果与 Apama Raman 等将烷基磷酸修饰于不锈钢表面测得的接触角值一致<sup>[14]</sup>.这也说明十烷基磷酸在不锈钢电极表面形成组装膜可能为单分子膜.表 1 所示,倘如修饰时间大于 4 h,则该电极表面接触角基本保持不变,这意味此时十烷基磷酸单分子膜已经达到饱和.

图 1 为不同组装时间得到的十烷基磷酸修饰不锈钢电极的极化曲线.由图可见,该修饰电极的腐蚀电位发生了明显正移,腐蚀电流减小,说明十烷基磷酸自组装膜为阳极型缓蚀剂,能够钝化不锈钢电极表面,增大阳极极化.此外,从组装 4 h(d)和组装 8 h(e)的修饰电极极化曲线可看出,二者  $E \sim \log i$  曲线基本一致,进一步佐证组装 4 h 修饰膜已达到饱和,与上面接触角实验结果吻合.据此,以

下实验将十烷基磷酸的修饰时间确定为 4 h

表 1 不同组装时间制备的修饰电极的接触角  
Tab 1 The contact angle of modified electrode with different time assembled in dodecyl sodium phosphonate

Assembled time/h	0	1	2	4	8
Contact angle/ $^\circ$	47 $\pm$ 4	71 $\pm$ 4	95 $\pm$ 4	106 $\pm$ 4	104 $\pm$ 4

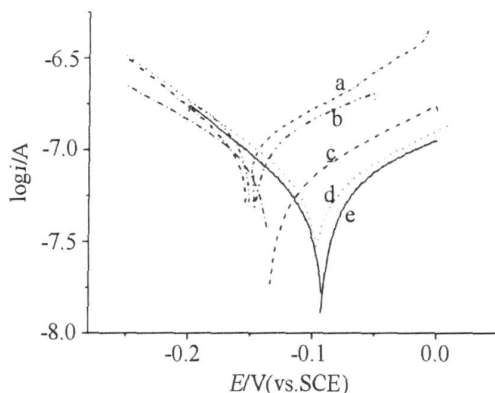


图 1 裸电极 (a) 和自组装修饰 1 h (b)、2 h (c)、4 h (d) 和 8 h (e) 的 Zr MonolayerSS 电极的极化曲线

Fig 1 The polarization curves of bare 304 stainless steel electrode (a) and MonolayerSS modified with 1 (b), 2 (c), 4 (d), 8 h (e)

### 2.2 DoublelayerSS 修饰电极的缓蚀性能

缓蚀剂自组装膜修饰电极的缓蚀效率与缓蚀剂的表面覆盖度有关<sup>[21]</sup>.图 2 示出裸不锈钢电极和 3 种修饰电极在 3% NaCl 溶液中的极化曲线.各电极的腐蚀电位,腐蚀电流和缓蚀效率等参数汇列于表 2.

表 2 不同修饰电极的电化学腐蚀参数的比较  
Tab 2 The electrochemical parameters of different modified electrodes

Electrodes	$I_p / \mu A \cdot cm^{-2}$	$E_{corr} / V (vs SCE)$	$\eta / \%$
Bare SS electrode	0.63	-0.157	
MonolayerSS	0.23	-0.096	59
Zr MonolayerSS	0.24	-0.088	62
DoublelayerSS			

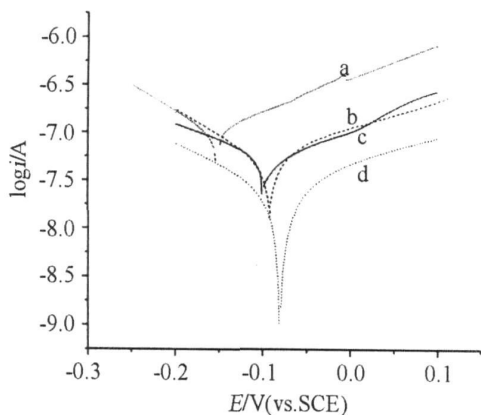


图 2 裸不锈钢电极 (a) 和 MonolayerSS (b), ZrMonolayerSS (c) 及 DoublelayerSS (d) 修饰电极在 3% NaCl 中的极化曲线

Fig 2 Polarization behavior of the bare electrode (a), MonolayerSS (b), ZrMonolayerSS (c) and DoublelayerSS (d) in 3% NaCl solution

由图 2 可见 MonolayerSS 和 ZrMonolayerSS 两修饰电极的极化曲线 (b, c) 大体相合, 而其缓蚀效率也无太大差别, 说明锆离子的引入对磷酸膜的表面覆盖度并没有明显的影响. 然而, 如果将 ZrMonolayerSS 进一步修饰成 DoublelayerSS 修饰电极, 则其缓蚀效率便由原先的 59% 提高到 79%. 这意味着此修饰电极的烷基磷酸修饰膜较之前两者更为致密, 覆盖度明显增大. 又从表 3 即可以看到, 当 MonolayerSS 修饰膜引入锆离子后, 该电极 ZrMonolayerSS 对水的接触角并未发生明显改变. 但对 DoublelayerSS 修饰电极, 则其接触角由原来的 103 降低到 57° 左右, 表明该修饰电极的亲水性

明显增加. 即锆离子引入使电极表面形成了磷酸双分子层, 亦电极由 MonolayerSS 时的单分子疏水性表面转变成 DoublelayerSS 时的双分子亲水性表面.

Apama Raman 等 [14] 依据漫反射傅里叶红外光谱确认, 有机磷酸在不锈钢表面形成的自组装单分子膜是通过磷酸分子的两个氧与不锈钢表面的氧化层以“双齿模式”成键 (如图 3A). 据本实验的接触角和极化曲线推测, 由于修饰电极引入的锆离子可与邻近的两个烷基磷酸分子发生键合, 从而使膜中的十烷基磷酸分子形成网状结构, 图 3B, C 分别示出 ZrMonolayerSS 修饰电极单层和 DoublelayerSS 修饰电极双层磷酸分子可能的网状结构.

表 3 不同修饰电极的接触角

Tab 3 The contact angle of different electrode

Electrodes	Contact angles/(°)
Bare electrode	47 ± 4
MonolayerSS	106 ± 4
ZrMonolayerSS	103 ± 4
DoublelayerSS	57 ± 4

### 3 结论

十烷基磷酸钠可作为阳离子缓蚀剂组装到不锈钢上, 形成具有抗蚀性的单分子自组装膜. 如在组装膜中引入锆离子, 可得到更加致密的双层十烷基磷酸修饰膜, 则不锈钢的抗蚀性将进一步增强.

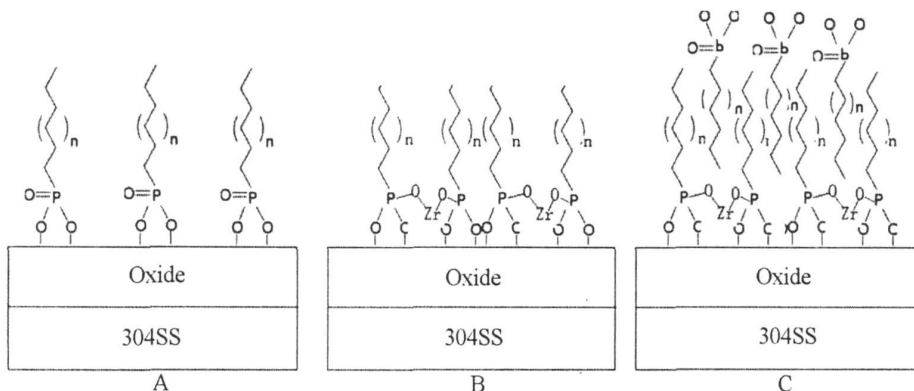


图 3 不同自组装膜结构示意图

Fig 3 Schematics of various electrodes modified with self assembled membrane

(A) MonolayerSS [12], (B) ZrMonolayerSS and (C) DoublelayerSS

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## Structure and Property of Molecular Self-assembled Membrane with Zirconium Ion

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**Abstract** According to the complex interaction between dodecyl phosphonate and stainless steel surface as well as the zirconium ion, the self-assembled monolayer and double-layer dodecyl phosphonate modified 304 type stainless steel electrode were prepared. The electrodes were characterized by static contact angles and electrochemical polarization methods. The results suggested that the double-layer modified stainless steel electrode had better corrosion inhibition effect than the monolayer modified electrode.

**Key words** self-assembled membrane; dodecyl sodium phosphonate; static contact angles; polarization curve; inhibitor