

DOI: 10.13208/j.electrochem.130811

Artical ID:1006-3471(2014)03-0277-05

Cite this: *J. Electrochem.* 2014, 20(3): 277-281

Http://electrochem.xmu.edu.cn

硫化银/凹凸棒的 Ag^+ 选择电极

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摘要: 以硝酸银、凹凸棒石和硫代乙酰胺为原料制得硫化银/凹凸棒($\text{Ag}_2\text{S}/\text{ATT}$)电极,并探讨了硫代乙酰胺配比、增塑剂用量、膜厚度以及溶液pH值等因素对电极性能的影响.结果表明,新型银离子选择电极有较好的能斯特响应,其响应斜率 $48.0 \text{ mV} \cdot \text{decade}^{-1}$, Ag^+ 浓度线性响应范围 $1.0 \times 10^{-1} \sim 1.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$.在 $\text{pH} = 2.0 \sim 8.0$ 溶液中该电极电势可稳定72 h,对常见阳离子如 Na^+ 、 Ca^{2+} 、 Fe^{2+} 、 Cu^{2+} 等呈现较强的抗干扰能力.

关键词: 凹凸棒石;银离子选择性电极;电活性物质;硫化银;电极稳定性

中图分类号: O646

文献标识码: A

硫化银(Ag_2S)载体选择性电极可检测 $\text{Ag}^{+[1-4]}$,且含纳米 Ag_2S 的银离子选择电极有较好的 Ag^+ 响应能力.但纳米 Ag_2S 粒子小,表面活性高,随时间增长会彼此团聚,从而影响了 Ag_2S 载体选择电极的稳定性^[5-7].

凹凸棒石(ATT)是一种富产的天然无机矿物,其单晶体呈束状结构,由平行于C轴的硅氧四面体双链组成,各个链间通过氧原子连接,上下交替排列.ATT链层单元和孔道相间排列,形成无数平行管状孔道,每个孔道的截面积大小近乎相等(约为 $0.38 \text{ nm} \times 0.63 \text{ nm}$),具有类分子筛性能.含ATT钙离子选择电极能有效提高电极的选择性和响应能力^[9-11].本文以ATT、硫代乙酰胺和硝酸银为原料,将 Ag_2S 负载在凹凸棒石表面,制得 $\text{Ag}_2\text{S}/\text{ATT}$ 电活性复合物银离子选择电极.ATT纳米结构表面可诱导硫代乙酰胺和硝酸银反应生成 Ag_2S 纳米粒子,并稳定纳米 Ag_2S 粒子尺寸及物理化学性质,从而改善 $\text{Ag}_2\text{S}/\text{ATT}$ 电活性复合物银离子选择电极的稳定性.此外,本文还测试了硫代乙酰胺浓度、膜厚度、pH、增塑剂与电极响应性能的关系.

1 实验

1.1 试剂与仪器

凹凸棒石,硫代乙酰胺,PVC粉末(平均聚合度1700~4000,相对分子质量约4.8万),邻苯二甲酸二丁酯(DBP),六偏磷酸钠,四氢呋喃,氯化钙均为分析纯试剂.

PHS-3B精密pH计,222型饱和甘汞电极,216型银电极,JSM-5610L扫描电子显微镜(日本,JEOL).

1.2 电活性 $\text{Ag}_2\text{S}/\text{ATT}$ 的制备

将已纯化的2 g ATT与30 mL $0.5 \text{ mol} \cdot \text{L}^{-1}$ 硝酸银溶液置于室温搅拌30 min,搁置24 h(ATT饱和吸附溶液 Ag^+)、过滤、蒸馏水洗涤及风干可得表面负载 Ag^+ 的ATT固体粉末(标记为 Ag^+/ATT).将0.5 g Ag^+/ATT 加入15 mL不同浓度的硫代乙酰胺的乙醇溶液,置于50 °C反应10 h,过滤,乙醇洗涤,干燥即得灰黑色的 $\text{Ag}_2\text{S}/\text{ATT}$ 固体物质.为证实 Ag_2S 的存在,向固体样品滴加硝酸,样品即由灰黑色变为白色,这是由黑色 Ag_2S 氧化成白色硫酸银所致.

1.3 功能膜

将250 mg电活性 $\text{Ag}_2\text{S}/\text{ATT}$ 、350 mg PVC和400 mg DBP混溶于四氢呋喃溶液,将该胶液置于培养皿,常温挥发,即得银离子选择膜.

1.4 电极组装

将离子选择膜胶粘至聚氯乙烯管端(内径8 mm,外径10 mm),在管内滴入含饱和氯化银的 $1.0 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$ NaCl水溶液,插入Ag电极,连接好导线,即得银离子选择膜电极,与饱和甘汞电极组成电池测试体系.

1.5 测试

将 $1.0 \times 10^{-1} \sim 1.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ AgNO_3 溶液,用 $1.0 \text{ mol} \cdot \text{L}^{-1}$ 硝酸和 $0.2 \text{ mol} \cdot \text{L}^{-1}$ NaOH溶液调节溶

液pH值(pH = 5.0). 测量时蒸馏水冲洗电极至电势稳定(每分钟变化0.5 ~ 1.0 mV), 分别取30 mL不同浓度的AgNO₃溶液置于50 mL烧杯中, 插入离子选择电极与参比电极记录体系平衡电势, 绘制电极电势(*E*)-Ag⁺浓度的负对数(-lg*C*_{Ag⁺})曲线, 得电极响应曲线. 每次测量前电极应彻底清洗.

2 结果与讨论

2.1 硫代乙酰胺浓度

图1显示5种不同电活性物电极在浓度 $1.0 \times 10^{-1} \sim 1.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ AgNO₃溶液(pH = 5)的电极电势曲线. 电活性物质分别为: Ag⁺/ATT(a), Ag₂S(b), 以及0.05 mol·L⁻¹ (c)、0.3 mol·L⁻¹ (d) 和1.0 mol·L⁻¹ (e) 硫代乙酰胺与Ag⁺/ATT反应所制得的Ag₂S/ATT. 从图1看出, Ag⁺/ATT电极的Ag⁺浓度响应斜率较低(约8 mV·decade⁻¹). 而不同硫代乙酰胺浓度的Ag₂S/ATT电极的响应性能也各不相同, 其中0.3 mol·L⁻¹硫代乙酰胺的Ag₂S/ATT电极响应斜率最大(48 mV·decade⁻¹), 电极响应时间最短(约3 s). 硫代乙酰胺能与硝酸银按以下反应式生成硫化银.



硫代乙酰胺在反应过程中, 硫离子缓慢地释放, 与溶液中Ag⁺发生反应生成纳米硫化银粒子, 这已被文献所证实^[12]. 而硫代乙酰胺仅与硝酸银反应所制得的Ag₂S电极响应斜率为39 mV·decade⁻¹, 与文献报道的纳米硫化银电极响应斜率值相当. 若ATT与Ag⁺混合, 其孔道内表面的负电荷和羟基能吸附银离子渗入至ATT纳米孔道内, 硫代乙酰胺与ATT孔道内Ag⁺发生反应生成硫化银. 与Ag₂S电极相比, Ag₂S/ATT电极响应斜率更大, 线性更好. 可推测在ATT孔道内的硫化银粒子更小, 表面活性更高, 粒度也更均匀. 硫代乙酰胺浓度太大(1.0 mol·L⁻¹)或太小(0.05 mol·L⁻¹), 其电极电势响应斜率均较小. 由于高浓度硫代乙酰胺生成的硫化银颗粒过大, 低浓度时生成的硫化银颗粒量又太少, 故二者Ag₂S/ATT电极响应斜率趋小. 图2给出了由0.3 mol·L⁻¹硫代乙酰胺制得的Ag₂S/ATT的扫描电镜照片. 纤维状的固体为ATT, 其表面不存在较大的固体颗粒. ATT存在下硫代乙酰胺与硝酸银反应所制得的Ag₂S可能以纳米级大小存在于ATT孔洞内外表面.

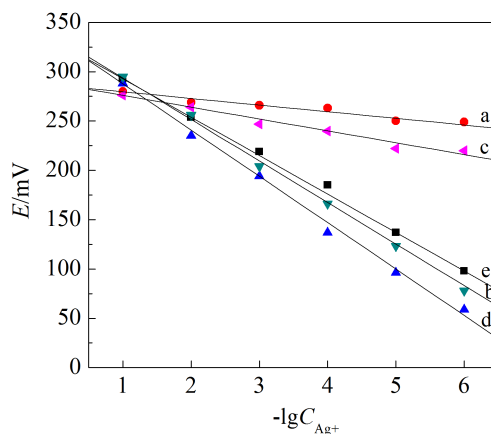


图1 银离子选择膜电极在AgNO₃溶液的*E*-(-lg*C*_{Ag⁺})曲线

a. Ag⁺/ATT; b. Ag₂S; c. 由0.05 mol·L⁻¹硫代乙酰胺制得的Ag₂S/ATT; d. 由0.3 mol·L⁻¹硫代乙酰胺制得的Ag₂S/ATT; e. 由1.0 mol·L⁻¹硫代乙酰胺制得的Ag₂S/ATT

Fig. 1 *E*-(-lg*C*_{Ag⁺}) curves of silver ion selective membrane electrodes in AgNO₃ solution, and the ionophores in the silver ion selective membrane electrodes are Ag⁺/ATT(a), Ag₂S(b), and Ag₂S/ATT composites prepared from different concentrations of thioacetamide solutions including 0.05 mol·L⁻¹ (c), 0.3 mol·L⁻¹ (d), and 1.0 mol·L⁻¹ (e)

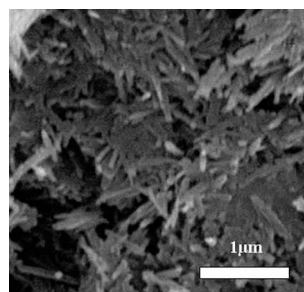


图2 Ag₂S/ATT复合物的扫描电镜照片

Fig. 2 SEM image of Ag₂S/ATT composite

2.2 增塑剂和膜厚度

本文PVC功能膜包含DBP和Ag₂S/ATT电活性物质, 须考虑电活性物质与增塑剂之间的相互作用^[13-14]. 图3给出DBP增塑剂在电活性物质含量不变的情况下, 功能膜含400 mg(a)、800 mg(b)、1200 mg(c)DBP的Ag₂S/ATT电极电势*E*-(-lg*C*_{Ag⁺})曲线(pH = 5.0). 从图3可看出, 不同含量DBP增塑剂的3支电极响应能力基本相似. 作者也制备了功能膜含200 mg DBP的Ag₂S/ATT电极, 该电极电势对(-lg*C*_{Ag⁺})的曲线线性关系较差, 故选取图3中最少

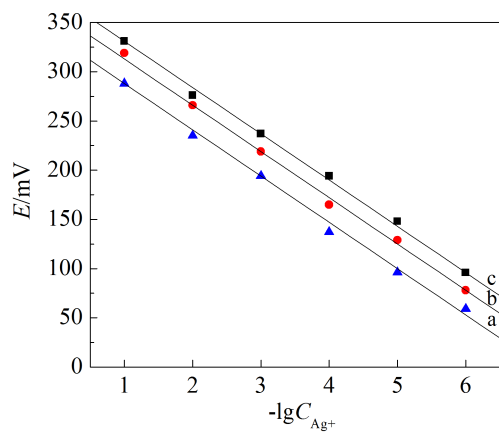


图3 400 mg(a)、800 mg (b)和1200 mg(c) DBP含量的银选择膜电极的 E - $(-\lg C_{Ag^+})$ 曲线

Fig. 3 E - $(-\lg C_{Ag^+})$ curves of silver ion selective membrane electrodes with the amounts of DBP being 400 mg (a), 800 mg (b) and 1200 mg (c)

用量为400 mg DBP制备Ag₂S/ATT电极.

不同膜厚度 (0.1 mm、0.3 mm、0.5 mm) 的电极, 其电势影响不明显. 当银电极浸入测试液中, Ag⁺向银电极表面扩散进入膜相, 形成双电层, 该界面电位与溶液中银离子的活度有关, 与膜厚度无关. 另外, 膜内Ag⁺的扩散电位也影响电极的总电势, 故0.1 mm~0.5 mm的不同厚度膜内扩散电势差别不大. 图4为银电极膜表面的扫描电镜照片. 从照片看出, 电极膜表面的PVC聚合物呈层状叠加分布, 不同层之间有较明显的带状断裂带, 膜表面还均匀分布着直径约1 μm未溶解的PVC颗粒.

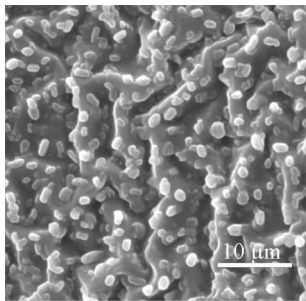


图4 电极膜表面的扫描电镜照片
Fig. 4 SEM image of the surface of electrode film

2.3 电极稳定性和溶液pH值

图5显示Ag₂S(a)、Ag₂S/ATT(b)电极的 E - t 曲线. 从图5看出, Ag₂S/ATT电极72 h电极电势漂移2 mV左右, Ag₂S电极电势下降幅度达12 mV, 这说

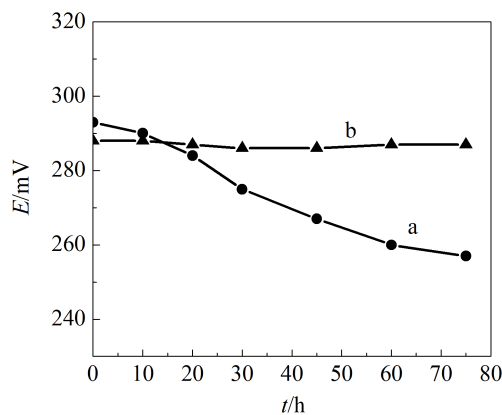


图5 Ag₂S(a)和Ag₂S/ATT(b)电极的 E - t 曲线
Fig. 5 E - t curves of silver electrodes in which ionophores are Ag₂S (a) and Ag₂S/ATT (b)

明纳米孔道结构的ATT所负载的硫化银有好的稳定性^[15].

图6给出在 $1.0 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$ (a) 和 $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (b) AgNO₃溶液中Ag₂S/ATT电极电势 E -pH曲线. 从图6看出, 在pH = 2.0~8.0的Ag⁺溶液电极电势(E)均较稳定. 而在酸性较强(pH < 2.0)溶液, 电极电势趋于升高, 在碱性较强(pH > 8.0)溶液, 电极电势下降. 溶液pH < 2.0时, 复合物电活性物质的ATT粘土骨架带负电荷, 可吸附溶液带正电荷H⁺, 该电活性银电极响应于溶液H⁺浓度. H⁺浓度增大, 电极电势上升. pH增至8.0时, Ag⁺易形成AgOH及Ag₂O沉淀, Ag⁺浓度减小, 电极电势下降.

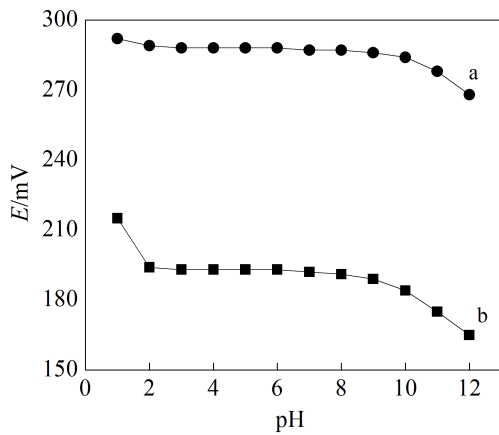


图6 Ag₂S/ATT电极在 $1.0 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$ (a) 和 $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ (b) AgNO₃溶液的 E -pH曲线
Fig. 6 E -pH curves of the Ag₂S/ATT electrodes in AgNO₃ solution with different concentrations
a. $1.0 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$; b. $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$

2.4 电极选择性

对以Ag₂S/ATT为电活物银选择电极,采用“分别溶液法”^[16]测定常见阳离子对Ag⁺的电极选择系数。“分别溶液法”即干扰离子和被测银离子在相同活度(如1.0 × 10⁻⁴ mol·L⁻¹和1.0 × 10⁻⁶ mol·L⁻¹)下,分别测定各离子溶液的电极电势,结合公式

$$\lg K_{\text{Ag}^+/\text{J}^{n+}} = \frac{(E_j - E_{\text{Ag}^+})}{0.059 Z_j} - \frac{\lg a}{Z_j} (Z_j - Z_{\text{Ag}^+})$$

计算电极选择系数。Ag⁺的Ag₂S/ATT的电极选择系数列于表1,lgK_{Ag⁺/Jⁿ⁺}越小,干扰离子(Jⁿ⁺)对电极Ag⁺的浓度测定干扰就越小^[16]。从表1可以看出,碱金属、碱土金属离子干扰能力较弱,Al³⁺、Mg²⁺、Zn²⁺等有部分干扰能力,Hg²⁺干扰能力最强。这与硫代乙酰胺的胺基基团能否与金属离子配位有关,硫代乙酰胺的硫原子可与吸附在凹凸棒石表面的银离子相互作用,使得硫代乙酰胺接枝于ATT表面,硫代乙酰胺的胺基则与溶液中金属离子相互作用,两者相互作用的强弱将影响Ag₂S/ATT电极的选择性。部分金属离子与氨形成的一级配合物的稳定常数顺序为Mn²⁺ < Fe²⁺ < Zn²⁺ < Ni²⁺ < Cu²⁺ < Hg²⁺,电极抗干扰能力与该稳定常数的排序大致相同。若排序不同,可能是由于还受重金属干扰离子与电活性Ag₂S/ATT的硫原子作用所致。

表1 Ag₂S/ATT电极的选择系数

Tab. 1 Selectivity coefficient lgK_{Ag⁺/Jⁿ⁺} of Ag₂S/ATT electrode

Ion(J ⁿ⁺)	lgK _{Ag⁺/Jⁿ⁺}	Ion(J ⁿ⁺)	lgK _{Ag⁺/Jⁿ⁺}
NH ₄ ⁺	-5.63	Mn ²⁺	-4.50
Na ⁺	-5.44	Zn ²⁺	-3.56
Ca ²⁺	-5.32	Fe ²⁺	-3.48
K ⁺	-5.11	Ni ²⁺	-3.22
Mg ²⁺	-5.01	Cu ²⁺	-3.01
Al ³⁺	-4.91	Hg ²⁺	-2.88

3 结 论

由硝酸银、凹凸棒石、硫代乙酰胺制得Ag₂S/ATT复合物,制备以该复合物为电活物的银离子选择电极。由0.3 mol·L⁻¹硫代乙酰胺制备的电极在1.0 × 10⁻¹ ~ 1.0 × 10⁻⁶ mol·L⁻¹ Ag⁺溶液中有较好的线性响应,响应时间3 s。增塑剂量及膜厚度对

电极的响应斜率的变化不明显。pH值2 ~ 8区间,电极电势可以稳定72 h。电极对常见的碱和碱土金属有强抗干扰能力,过渡金属离子干扰能力与该金属离子的氨配合物稳定常数有关。Ag₂S/ATT电活物银选择电极比Ag₂S电活物电极有更高的响应斜率及更高的稳定性。而与合成复杂的杯芳烃衍生物电活物银选择电极(响应斜率约50 mV·decade⁻¹,响应时间约15 s,适用pH范围2.5 ~ 6.5)^[17]相比,电极性能近似,但Ag₂S/ATT电活物合成更简单,电活物合成成本更低。

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A New Silver Electrode Based on the Composite Silver Sulfide/Attapulgite as Ionophore

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Abstract: A novel silver ion selective electrode with its ionophore being a kind of organic/inorganic composite composed of silver sulfide and attapulgite has been prepared. Attapulgite is a type of natural inorganic polymer which has some properties similar to zeolite, such as a higher specific surface area and plenty of intercrystalline cavities. In this work, the silver ions were firstly adsorbed in the micropores of the attapulgite, then thioacetamidetiny was selected to mix with the prepared silver ions/ attapulgite composite. Owing to the existence of sulfur atoms in the structure of thioacetamide molecules, thioacetamide molecules can react with the silver ions/attapulgite composite so that tiny silver sulfide particles were formed within the pores of attapulgite. Experimental results showed that the prepared silver ion selective electrode with the silver sulfide/attapulgite composite as the ionophore exhibited the better linear responses toward silver ion measured and the quick response time (about 3 s). And effects of the concentration of thioacetamide on starting material, depth of electrode membrane, amount of plastic agent, pH of measured solution on the silver electrode performance had been investigated in this work. Experimental results also proved that the silver electrode displayed a proximate Nernst response with a linear slope of 48 mV·decade⁻¹ in the silver concentrations from 1.0×10^{-1} to 1.0×10^{-6} mol·L⁻¹. Within the range of pH = 2.0 ~ 8.0, the potential of the silver electrode had a better stability in 72 h. Also, the silver electrode showed better anti-interference in the measured solution containing some common metal ions like Na⁺, Ca²⁺, Fe²⁺ and Cu²⁺ etc.

Key words: attapulgite; silver ion selective electrode; ionophore; silver sulfide; electrode stability