Electro-assisted formation of organothiols self-assembled monolayers on polycrystalline copper surfaces

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Electro-assisted formation of organothiols self-assembled monolayers on polycrystalline copper surfaces

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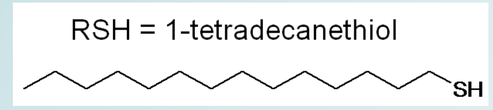
General context: organothiols films grafted on copper

- **Organothiol *Self-Assembled Monolayers* (SAMs)** can be successfully adsorbed on noble (Au) and **oxidizable metals** (Cu, Zn, Ni). They can be used as protective coatings against corrosion, lubricants, lithographic patterns, molecular (bio)sensors, … [1]
- **Oxidation state of the substrate surface** is a key factor for the SAMs formation => an **electrochemical reduction pretreatment of the Cu oxides layer** can be exploited to form **reproducible high quality films** [2].
- **Molecular adsorption process** has an important impact on the SAMs characteristics: ***passive* self-assembly** (open circuit potential) **vs. *active* electro-assisted assembly** (cathodic polarization of Cu) [3].

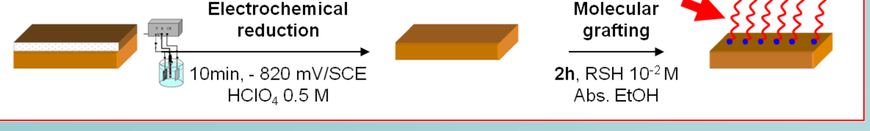
Two experimental approaches and methodologies

RSH = 1-tetradecanethiol

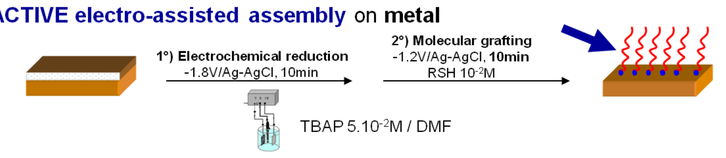


PRE-TREATMENT
Mechanical polishing, UV/O_3 (10min), sonication in abs. EtOH (10min), drying and storing under N_2

PASSIVE self-assembly on **metal**



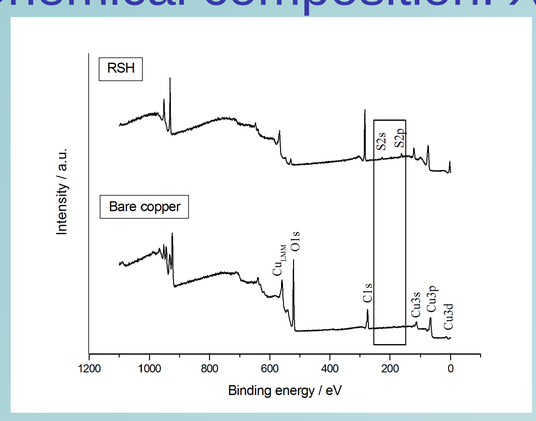
ACTIVE electro-assisted assembly on **metal**

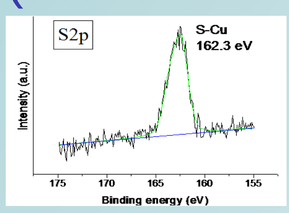


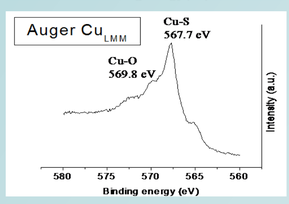
POST-TREATMENT
Sonication in abs. EtOH (10min), drying and storing under N_2

Results and discussion

Chemical composition: *XPS* (*active* method)



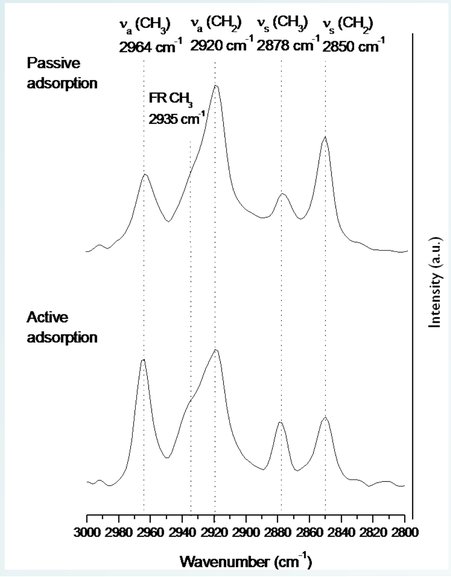




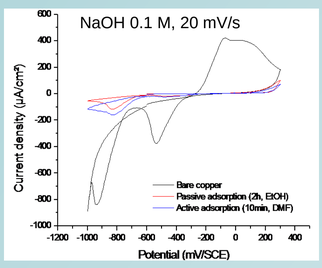
- **Confirmed grafting**: S2s & S2p, C1s increases
- **Thiolate S-Cu bond** at 162.3 eV => no unbound thiol (164 eV) or oxidized species (> 164 eV)
- **Reduction of the oxides layer** (Auger Cu_{LMM})
- **Hydrocarbon contaminations**: CH/S = 25.6 – th. = 13

Structure and organization: *PM-IRRAS*

- **$\nu_a(CH_2)$ = 2920 cm^{-1}** and **$\nu_s(CH_2)$ = 2850 cm^{-1}** => in both cases, **densely packed monolayers** with alkyl chains in a ***trans* zig zag conformation**
- **Intensity of CH_3 bands more important with the active adsorption process => modification of the alkyl chain inclination and orientation relative to the substrate surface** due to the cathodic polarization of Cu

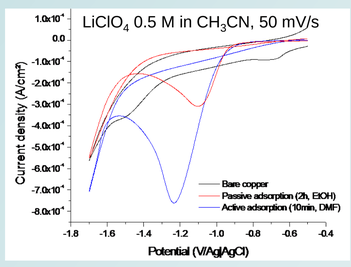


Electrochemical stability (CV, cath. desorption)

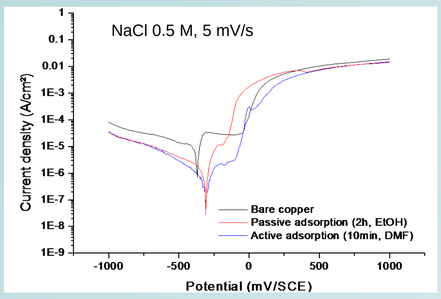


	Blocking ratio (%)	E_{des} (V/Ag-AgCl)
Passive adsorption (2h, EtOH)	97	- 1.14
Active adsorption (10min, DMF)	97	- 1.23

=> **High anodic and cathodic stabilities**



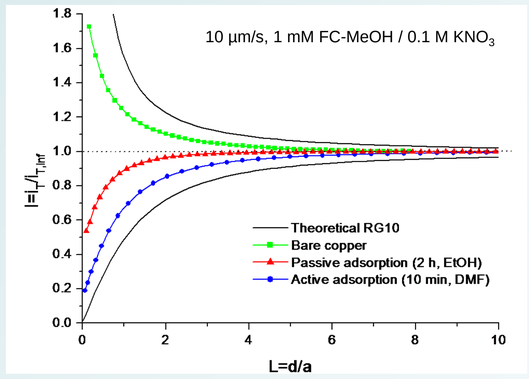
Protection against corrosion (pol. curves)

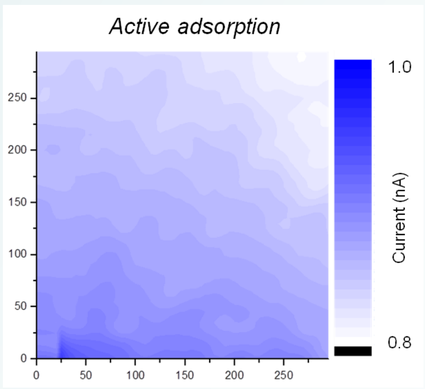


	I_{cor} (A/cm²)	E_{cor} (mV/SCE)	E_{pit} (mV/SCE)
Bare copper	6.4 10^{-6}	- 374	- 45
Passive adsorption (2h, EtOH)	4.4 10^{-7}	- 308	- 95
Active adsorption (10min, DMF)	4.1 10^{-7}	- 312	- 165

=> **« Mixed-to-anodic » protection**
=> Significant **decrease of I_{cor}**

Local characterization: *SECM*





	I/I_0
Bare copper	1.73
Passive adsorption (2h, EtOH)	0.54
Active adsorption (10min, DMF)	0.19

=> **Active adsorption reinforces the insulating features of the grafted films** (decreasing of I/I_0)
=> **Homogeneous surfaces**

Conclusions and perspectives

- **Efficiency of *active* electro-assisted adsorption of organothiols on copper** => formation of SAMs with **excellent properties of organization**, **protective against corrosion**, **with high electrochemical stability**, and formed with a **significant saving of time** comparatively to the *passive* methodology (10min vs. 2h).

- Perspectives: variation and optimization of experimental conditions with other substrates and surfactants [3], use of ionic liquids (to reduce hydrocarbon contaminations), …

References

[1] P.E. Laibinis, G.M. Whitesides, D.L. Allara, Y.T. Tao, A.N. Parikh, R.G. Nuzzo, *J. Am. Chem. Soc.* **1991**, *113*, 7152-7167; G. Fonder, F. Laffineur, J. Delhalle, Z. Mekhalif, *J. Colloid. Interf. Sci .* **2008**, *326*, 333-338.

[2] Z. Mekhalif, F. Sinapi, F. Laffineur, J. Delhalle, *J. Electron. Spectrosc.* **2001**, *121*, 149-161; J. Denayer, J. Delhalle, Z. Mekhalif, *J. Electroanal. Chem.* **2009**, *637*, 43-49; G. Fonder, C. Volcke, B. Csoka, J. Delhalle, Z. Mekhalif, *Electrochim. Acta* **2010**, *55*, 1557-1567.

[3] A. Maho, J. Denayer, J. Delhalle, Z. Mekhalif, *Electrochim. Acta* **2011**, *56*, 3954-3962.

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