MODIFICATION OF SELF-ASSEMBLED LAYER OF ELAIDIC ACID ON COPPER BY GAMMA IRRADIATION

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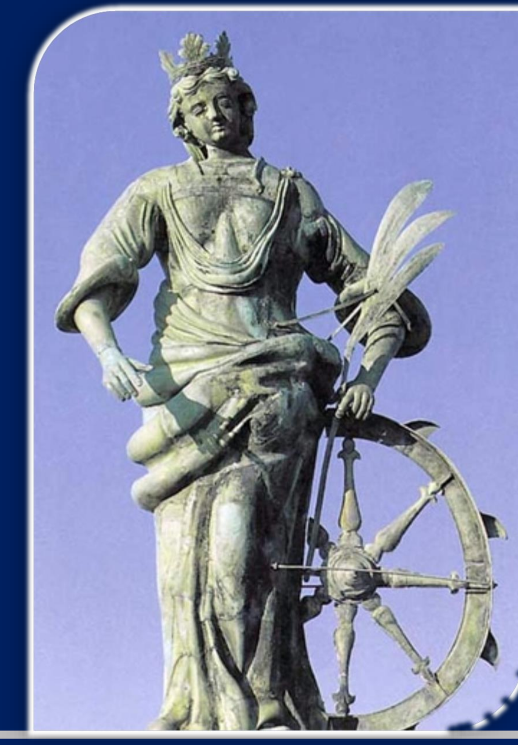
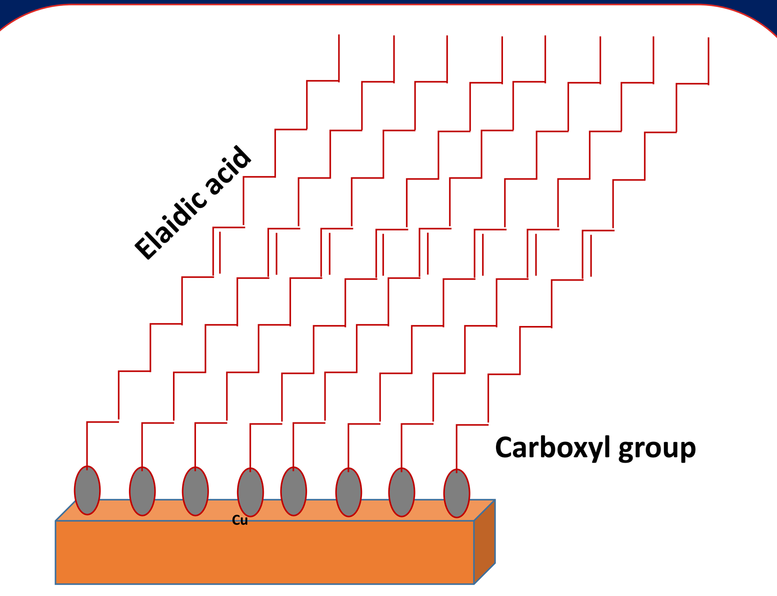


INTRODUCTION

Copper has been widely used in construction of sculptures and other works of art for ages. When exposed to air a thin oxide layer is formed. This layer offers natural protection to copper. Due to increased environmental pollution copper's natural protection is not enough. In order to preserve cultural heritage in these conditions it is necessary to apply additional protection from corrosion.

Formation of a thin self-assembled protective film (SAM) on the surface of the natural oxide film is a good and practical way to enhance the metal's natural protective properties. Fatty acids are non-toxic compounds which have an affinity for adsorbing on metals with their hydrophobic end, the carboxyl group. The other end of fatty acids, the methyl group, has hydrophobic properties and when adsorbed on the metal surface it makes the whole surface of the metal appear hydrophobic. Thus by blocking access for water to the surface the dissolution of the metal is disabled [1]. Elaidic acid (EA) is a monounsaturated long-chain fatty acid with a *trans* geometrical configuration. Because of the specific shape that it has thanks to the *trans* form of the double bond its molecules are close-packed on the surface of copper making the coating very compact and water difficult to approach the surface [2]. The EA coating is convenient to be used on cultural heritage, because it is very thin and does not change the appearance of the surface. Unfortunately, when exposed to urban outdoors, i.e. to rain and the sun fatty acids tend to degrade and to wash-off and so the protective properties of the SAM are not long-lasting.



Close-packed monolayer of elaidic acid on the surface of copper.

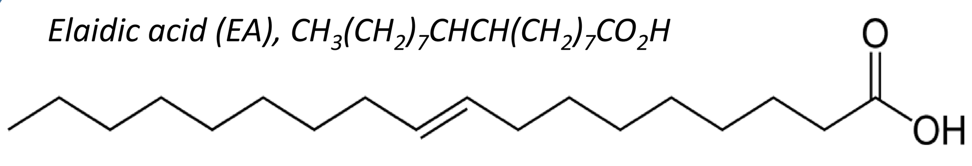
Gamma irradiation is penetrating electromagnetic ionizing radiation arising from the radioactive decay of atomic nuclei. Gamma irradiation can be used to induce changes and to alter the properties of materials or even to produce new materials.

The aim of this research is to investigate the possibility of using ionizing radiation to modify the structure of the elaidic acid SAM on copper's surface, i.e. to crosslink the EA molecules adsorbed on the surface. By crosslinking the coating would become more stable and durable, while it still would be only physically adsorbed on the surface.

EXPERIMENTAL

Electrode: Cu (99.9%)
Counter electrode: Pt electrode
Reference electrode: SCE
Electrolyte: 0.5 g/L $NaHCO_3$ + 0.5 g/L $NaNO_3$ + 0.5 g/L Na_2SO_4 at pH5
Inhibitor: Elaidic acid (EA) dissolved in ethanol at c = 0.01 mol/L

Elaidic acid (EA), $CH_3(CH_2)_7CHCH(CH_2)_7CO_2H$



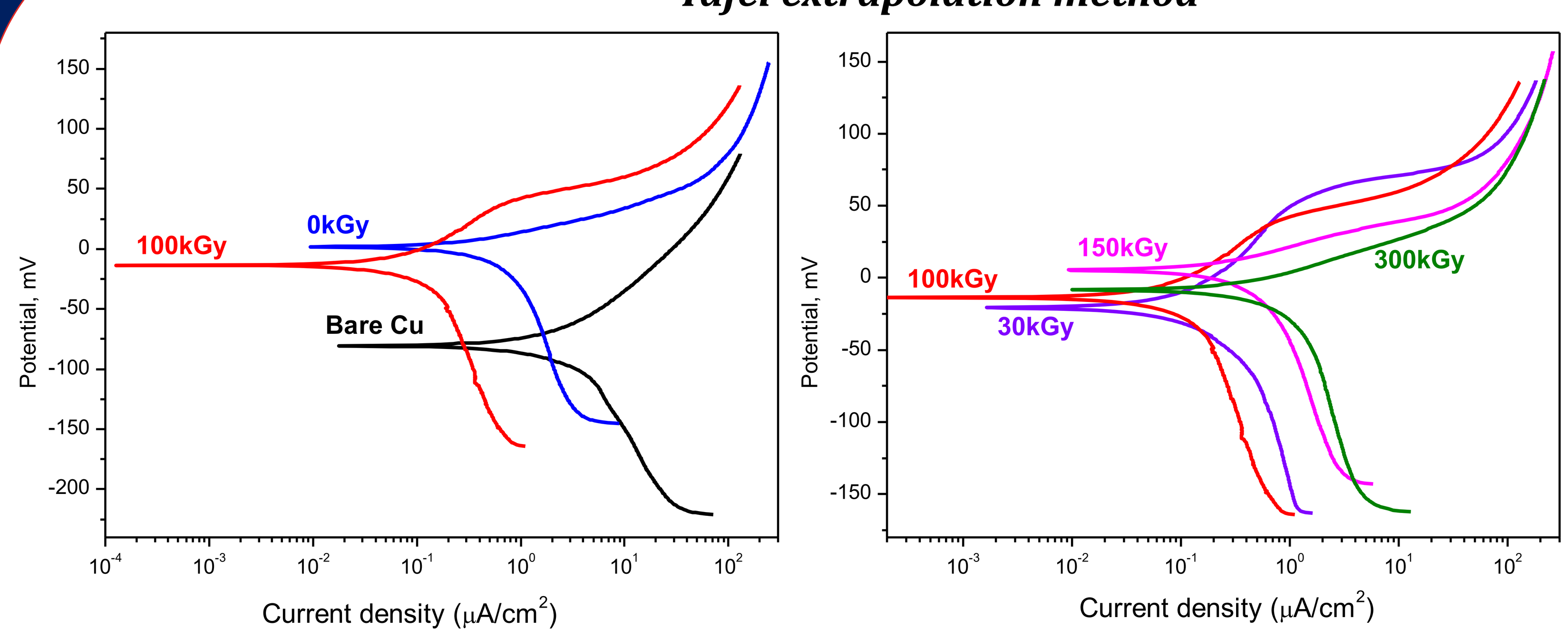
Preparation of EA treated samples:
- Copper samples heated in furnace for 4h at 75 °C
- Immersed in EA/EtOH for 24h at 40 °C
- Drying in furnace at 50 °C

Irradiation:
- Gamma irradiated in closed system, air purged by N_2 and irradiated with different doses at 7.3 Gy/s
- The dose rate was established using an ethanol-chlorobenzene (ECB) dosimetry system (10% vol. chlorobenzene in 96% ethanol [3]) and the preparation procedure according to ISO/ASTM 51538:2017 [4].

Sample labels:
- "Bare copper" – only polished copper
- "0kgy" – EA treated copper without irradiation treatment
- "10kGy", "30kGy"..."300kGy" – EA treated copper irradiated with the indicated doses

RESULTS

Tafel extrapolation method

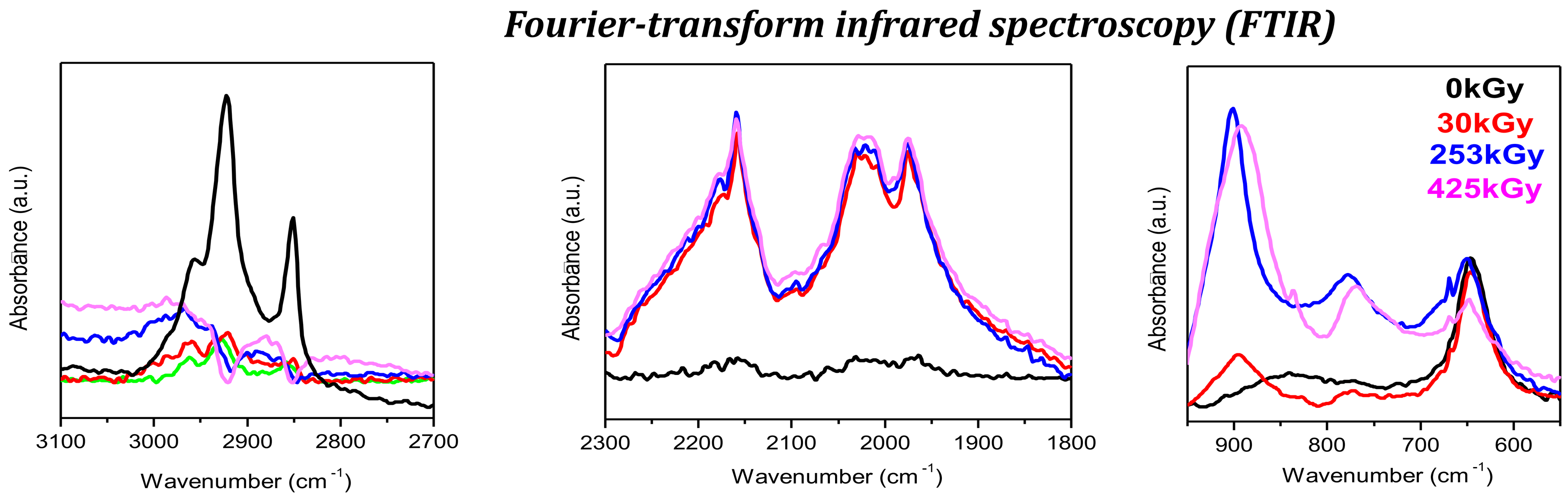


	D, kGy	E_{corr}, mV	b_a, mV dec⁻¹	$-b_c$, mV dec⁻¹	j_{corr}, μA/cm²	*IE*, %
-	-	-60±20	81±30	223±30	4.236±0.761	-
Elaidic acid (EA)	0	1±2	33±3	264±3	0.814±0.078	80.8
	10	3±1	40±9	190±8	0.624±0.122	85.3
	30	-19±2	107±13	231±15	0.384±0.093	90.9
	100	**-16±2**	**81±4**	**237±32**	**0.283±0.095**	**93.3**
	150	-3±8	50±22	205±10	0.658±0.130	85.2
	300	-6±2	34±1	225±19	0.946±0.010	77.7

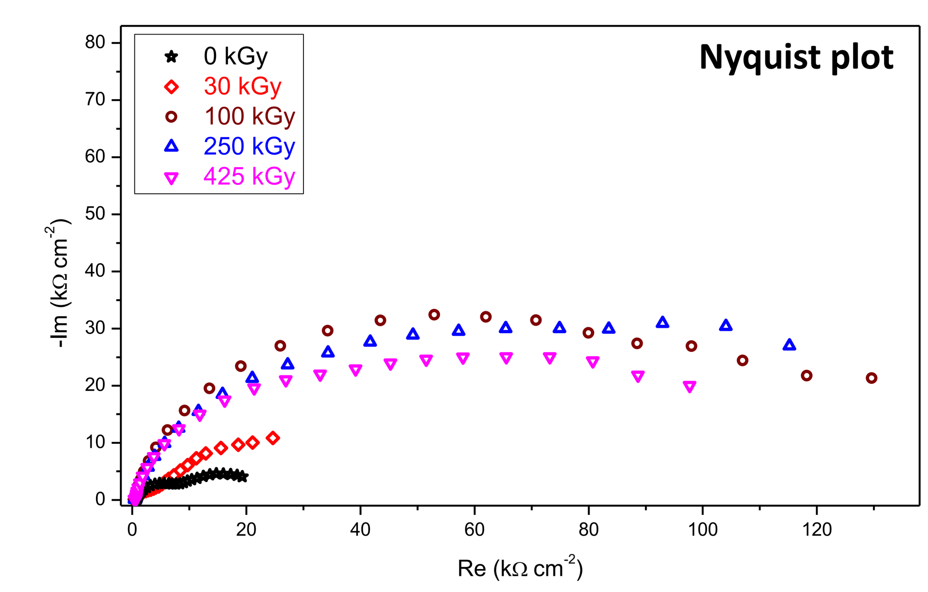
$$IE = \frac{j^0_{corr} - j_{corr}}{j^0_{corr}} * 100\%$$

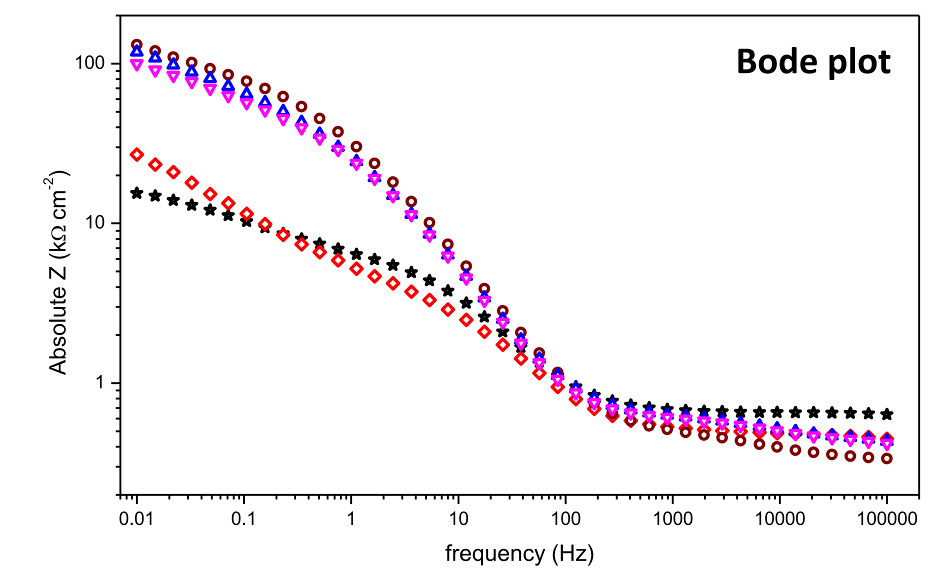
IE [%] – inhibitor efficiency
j^0_{corr} [μA/cm²] – corrosion current density of non-treated copper
j_{corr} [μA/cm²] – corrosion current density of copper treated with EA

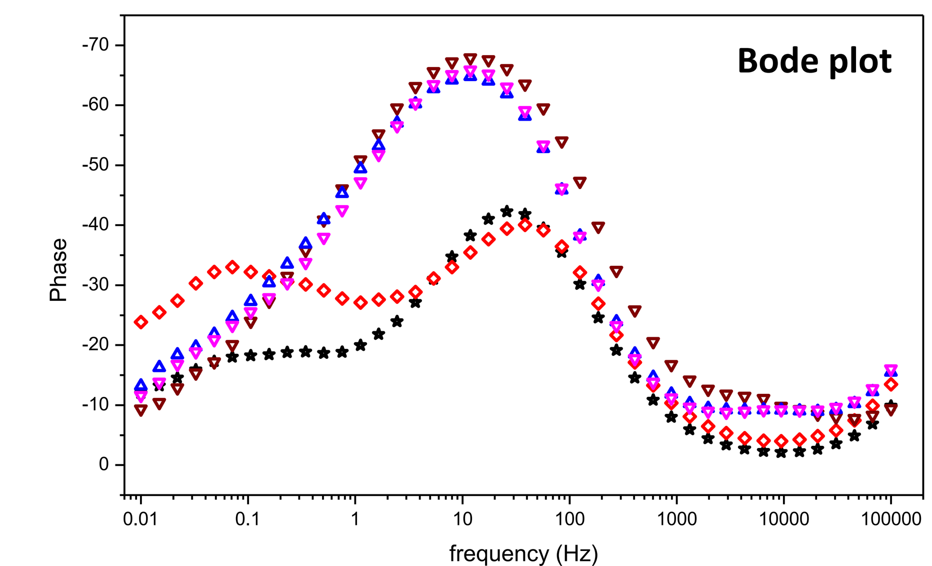
Fourier-transform infrared spectroscopy (FTIR)



Electrochemical impedance spectroscopy (EIS)







CONCLUSIONS

- The possibility to use gamma irradiation for crosslinking of self-assembled molecules (SAM) of a fatty acid on copper was investigated. Elaidic acid (EA) is a monounsaturated long-chain fatty acid with a *trans* geometrical configuration which self-assembles on copper's surface when diluted in ethanol and forms a close-packed surface film which upon irradiation could be crosslinked.
- It has been established that upon irradiation the protective efficiency of the EA coating significantly increases in a solution simulating urban rain and that its chemical structure has changed.

Tafel	❑ Presence of EA on the surface shifts the polarization curves towards the more noble direction, i.e. towards higher corrosion potentials and the current densities to lower values. Upon irradiation the anodic tafel slope increases indicating that irradiation slowed down the anodic process. ❑ The best protective effect was observed when the film was irradiated with 100 kGy. The efficiency of the SAM increased upon irradiation from 80.8 % to even 93.3 % at 100 kGy, while the corrosion current density decreased from 814 to 283 nA/cm².
EIS	❑ After irradiation the semicircles in the Nyquist plot increased indicating that irradiation increased the system's resistance towards corrosion. ❑ The non-irradiated samples and samples irradiated with 30 kGy show two time constants in the Bode plot (Phase-Frequency): one attributed to the resistance of electrons or ions through the coating, i.e. "pores", R_c, and the other attributed to capacitance of the layer, C_{dl}. ❑ Upon irradiation with doses 100 kGy and higher only one phase constant can be seen which indicates that the coating is complete and homogeneous and that the metal is well separated from the aqueous phase [5].
FTIR	❑ The C-H stretching modes are represented by peaks in the 2800-3000 cm⁻¹ region. The decrease of these peaks indicates that EA has reacted [6]. ❑ Clear presence of various new peaks can be seen in the FTIR spectra upon irradiation at all doses.

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