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Editors:
Desimir Marković
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ELECTROCHEMICAL POLYMERIZATION OF PROTECTIVE POLYANILINE COATING ON COPPER

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Abstract

Conditions for galvanostatic electrochemical polymerization of protective polyaniline (PANI) coating on copper were investigated. It was observed that uniform film of PANI on copper could be obtained with current density of 1.25 mA cm^{-2}, from aqueous solution containing 0.3 mol dm^{-3} sodium benzoate and 0.2 mol dm^{-3} aniline monomer. Corrosion behavior of PANI coated copper in 3.0 % sodium chloride solution was investigated using potentiodynamic and electrochemical impedance spectroscopy techniques. Thin (5 μm) PANI coating provided efficient protection (app. 96%), while unusual impedance behavior comparing to conventional organic coatings, was attributed to dedoping of benzoate anions from the coating.

Keywords: aniline, galvanostatic polymerization, copper, corrosion behavior

1. INTRODUCTION

Due to its high electrical and thermal conductivity and excellent formability, copper and its numerous alloys are widely used in industrial applications. Although copper exhibits good corrosion resistance, it corrodes in variety of aggressive environments. The corrosion protection strategy of copper and its alloys is usually based on usage of organic compounds (inhibitors) mainly benzotriazoles, animotriazole and derivates. Inhibitors provide good protection, however they are quite toxic. In last decade, electroconducting polymers (EPP), in first place polypyrrole (PPY) and polyaniline (PANI) were investigated in various practical fields, including environmental friendly corrosion protection. Although both chemical and electrochemical oxidative polymerization are usable in obtaining ECP, electrochemical synthesis is favorable permitting direct polymer film synthesis on metal surface without oxidizing agent. Generally, the basic problem in electrochemical polymerization of ECP on copper is occurrence of two competitive processes on anode: electrochemical synthesis and deposition of ECP and dissolution of copper on potentials necessary to oxidize the monomer. Therefore, it would be necessary to use electrolytes that can passivate copper and permit electrochemical polymerization. Although PANI, due to lower price of its monomer seams more challengeable, most of the studies were devoted to use of PPY [1-3], and only few to application of PANI and derivates in corrosion protection of copper and its alloys [4].
Since, it is evident that there is interest in application of PANI in corrosion protection of copper, the aim of this work was to consider conditions for electrochemical synthesis of protective PANI on copper from sodium benzoate electrolyte, which was proven to be efficient electrolyte for electrochemical synthesis of PANI on steel and aluminum [5,6].

2. EXPERIMENTAL

Potentiodynamic anodic polarization curves of copper electrode were recording at scan rate 0.5 mV s^{-1}, in 0.3 mol dm^{-3} sodium benzoate without and with addition of 0.2 mol dm^{-2} aniline. Electrochemical synthesis of polyaniline (PANI) film on copper was performed by electrochemical polymerization from aqueous solution of 0.3 mol dm^{-3} sodium benzoate and 0.2 mol dm^{-3} aniline. The polyemrization of aniline on copper sheet (S = 2.0 cm^2). was achieved under galvanostatic conditions using current density range between 0.50 and 1.25 mA cm^{-2}. Before all experiments, copper electrode was first mechanically abraded by fine emery papers and then by polishing alumina on polishing cloths, traces of the polishing alumina were removed from the electrode surface ultrasonically. Potentiodynamic measurements and electrochemical impedance spectroscopy (EIS) were used for corrosion studies of copper electrode and PANI coated copper electrode in 3.0 % sodium chloride solution. In order to avoid the edge effects, the surface area of the copper and PANI coated copper electrode used in corrosion measurements was reduced to 1.0 cm^2. In all experiments standard three compartment electrochemical cell was used. Copper and PANI coated copper electrode served as working, standard calomel (SCE) as reference and platinum wire was used as counter electrode. EIS measurements were performed at open circuit potentials in the frequency range between 50 mHz and 100 kHz, while below 5 Hz the fast Fourier technique (FFT) was used. The EIS experiments were performed using PC controlled PAR263A potentiostat/galvanostat connected to PAR frequency response detector FRD100.

3. RESULTS AND DISSCUSION

3.1 Electrochemical polymerization

Optimal concentration of sodium benzoate for electrochemical polymerization of aniline on copper was estimated from previously recorded anodic polarization curves of copper electrode in different concentration of sodium benzoate. In order to monitor the course of anodic polymerization of aniline, anodic polarization curves of copper electrode in 0.3 mol dm^{-3} sodium benzoate with addition of 0.2 mol dm^{-3} aniline, were recorded and presented in Fig. 1.

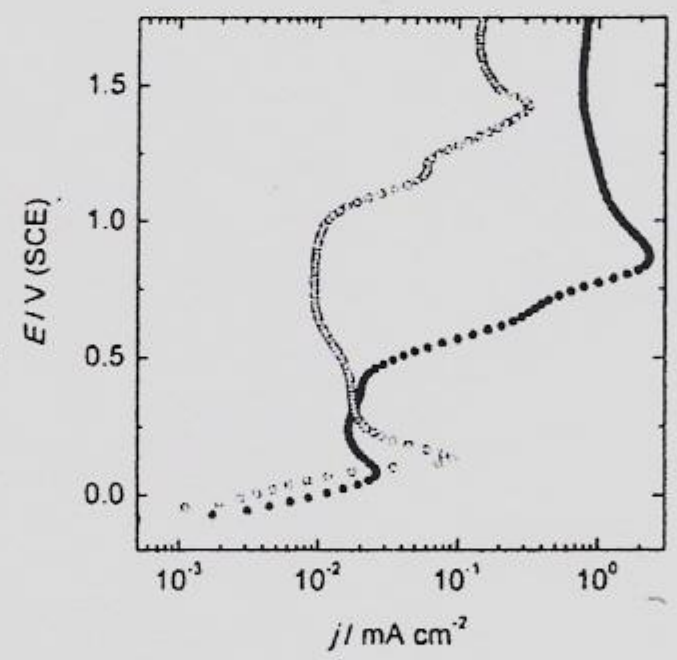

Figure 1. Potentiodynamic anodic polarization (v = 0.5 mV s^{-1}) curves of copper in: (○) - 0.3 mol dm^{-3} sodium benzoate and (●) - 0.3 mol dm^{-3} sodium benzoate and 0.20 mol dm^{-3} aniline

The presence of aniline shifted open circuit potential of copper for ~ 50 mV in the negative direction, connected to anodic inhibitory effect of absorbed aniline monomer. After short passivation of copper, in aniline containing electrolyte, polymerization started at potentials more positive than 0.4 V (SCE) and proceeded up to the potential of 2.5 V(SCE). The observed pick at ~ 0.7 V (SCE) could be connected to existence of polyaniline in the form of pernigraniline salt, at potentials more positive than ~ 2 V (SCE), slow oxygen reduction reaction was observed.

Chronopotentiometric (galvanostatic) curves of electrochemical polymerization of aniline on copper electrode from aqueous solution of 0.3 mol dm^{-3} sodium benzoate and 0.2 mol dm^{-3} aniline, using different current densities during 1000 s are given in Fig.2.

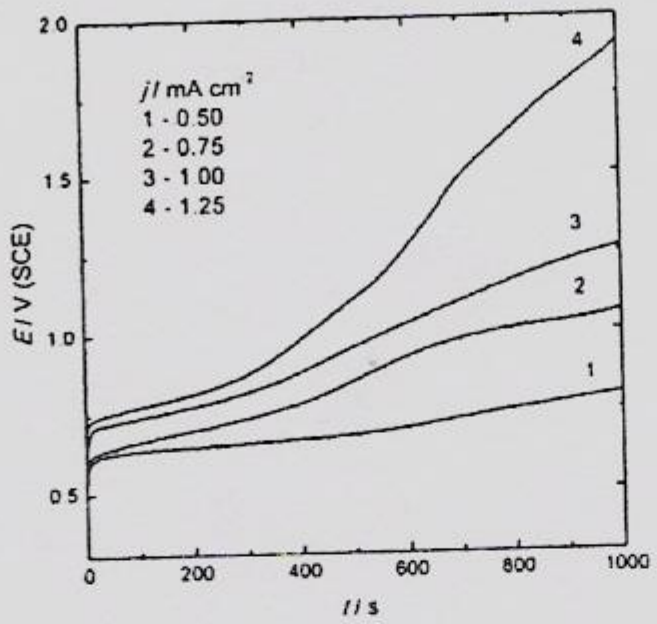

Figure 2. Galvanostatic polymerization of aniline on Cu electrode from 0.3 mol dm^{-3} sodium benzoate and 0.2 mol dm^{-3} aniline solutions using different current densities

Since, the completely uniform PANI films were obtained using higher current densities and in order to achieve lower extent of degradation, polymerization current density of 1.0 mA cm^{-2} was used in further experiments.

3.2 Corrosion studies

Potentiodymanic polarization curves (v = 0.5 mV s^{-1}) of copper and copper coated by electrochemically deposited PANI film, after 24 h of immersion in 3.0 % NaCl are given in Fig.3.

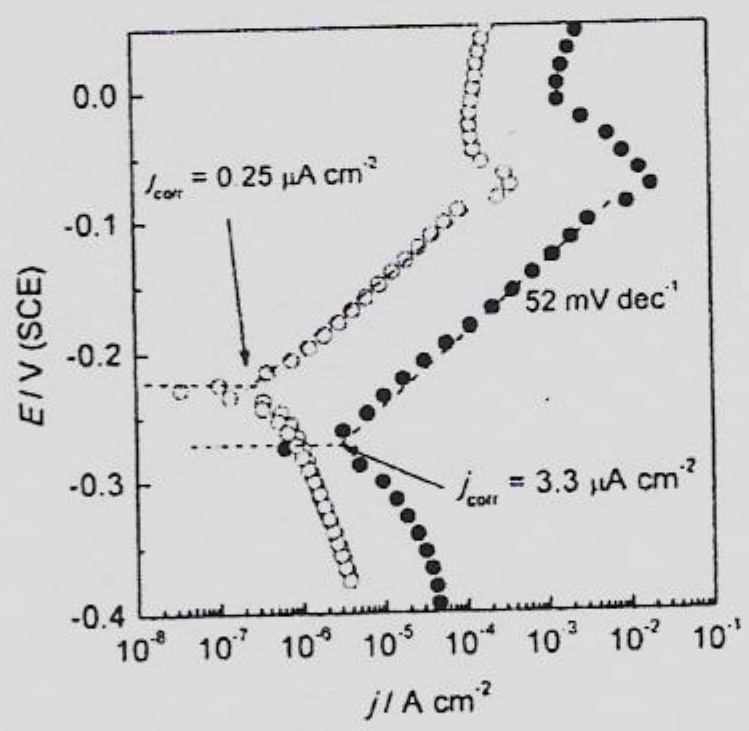

Figure 3. Potentiodynamic (v = 0.5 mV s^{-1}) polarization curves of: (●)- Cu and (○) – PANI coated Cu in 3.0 % NaCl

Anodic polarization curves of copper and PANI coated copper are both under activation control, characterized by the Tafel slope of ~ 54 mV dec^{-1}, connected to anodic dissolution of copper, while cathodic polarization curves are under mixed activacion-diffusion control of oxygen reduction. The corrosion potential of pure copper was, E_{corr} = -0.270 V (SCE), while corrosion potential of PANI coated copper was E_{corr} = - 0.225 V(SCE). Corrosion current densities were determined as intercept of anodic Tafel lines with corrosion potential. The protection efficiency of PANI was estimated to 96 %.

Complex plane spectra of PANI coated copper taken at different times of exposure in 3.0 % NaCl are given in Fig.4, while the time dependences of the corresponding open circuit (corrosion) potential, at which the impedance spectra were given in Insert.

The overall impedance of PANI coated copper, unusually to conventional organic coatings, firstly increased. The increase of the impedance might be a consequence of cathodic dedoping of benzoate anions from PANI film, according to:

$$(PANI^{y+}(C_6H_5COO^-)_y)_n + nye \rightarrow (PANI)_n + ny\ C_6H_5COO^-$$

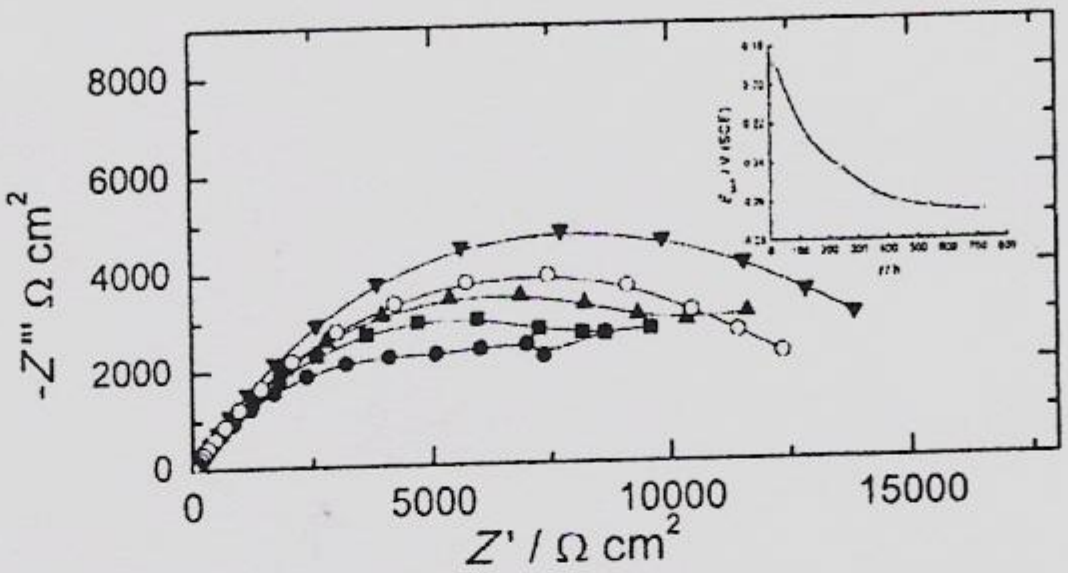

Figure 4. Complex plane impedance spectra of PANI coated Cu after:
(●) - 120 h, (■) – 240 h, (▲) – 360 h, (▼) – 540 h and (○) – 720h of exposure to 0.5 mol dm^{-3} NaCl.
Insert: Time dependences of corresponding open circuit potentials.

Dedoping lead the lost of the PANI film conductivity, reflected in the increase of the overall impedance. Since the shift of the open circuit potential to more negative values is characteristic of dedeoped state the observed decrease in corrosion potentials (Insert of Fig.4), also confirms the assumption of the dedoping process. After observed increase, the overall impedance of PANI started to decrease slowly, meaning that PANI started to act as conventional organic coating enabling barrier corrosion protection of the metal surface.

4. CONCLUSION

Electrochemical synthesis of PANI on copper was successfully performed from aqueous sodium benzoate solution containing aniline. PANI thin coating had provided high protection efficiency to copper. Based on potentiodynamic and EIS measurements, corrosion process of PANI coated copper in NaCl can be explained by the same processes of copper anodic dissolution and cathodic oxygen reduction occurring in parallel with slow cathodic dedoping of the benzoate anions from the PANI film, after dedoping, PANI coating started to act like conventional organic coating.

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