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Electrochemical and morphological characterisation of polyphenazine films on copper

Carla Gouveia-Caridade, Andreia Romeiro, Christopher M.A. Brett*

Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-535 Coimbra, Portugal

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ABSTRACT

The morphology of films of the phenazine polymers poly(neutral red) (PNR), poly(brilliant cresyl blue) (PBCB), poly(Nile blue A) (PNB) and poly(safranine T) (PST), formed by potential cycling electropolymerisation on copper electrodes, in order to reduce the corrosion rate of copper, has been examined by scanning electron microscopy (SEM). The copper surface was initially partially passivated in sodium oxalate, hydrogen carbonate or salicylate solution, in order to inhibit copper dissolution at potentials where phenazine monomer oxidation occurs, and to induce better polymer film adhesion. SEM images were also taken of partially passivated copper in order to throw light on the different morphology and anti-corrosive behaviour of the polyphenazine films. Analysis of the morphology of the polymer-coated copper with best anti-corrosive behaviour after 72 h immersion in 0.1 M KCl, Cu/hydrogen carbonate/PNB, showed that the surface is completely covered by closely packed crystals. By contrast, images of PST films on copper partially passivated in oxalate solution, that had the least protective behaviour, showed large amounts of insoluble corrosion products after only 4 h immersion in 0.1 M KCl.

1. Introduction

Electrochemical synthesis of conducting polymers on active metal electrodes has become a subject of multidisciplinary interest in the last few years, with increased significance for corrosion protection. The electrodeposition of conducting polymers on oxidisable metals is not easy, since thermodynamic data predict that the metal will dissolve before the oxidation potential of the monomer to initiate electropolymerisation is reached. Oxidation of the metal appears as a simultaneous and competitive process to formation of the polymer. Thus, it is necessary to find electrochemical conditions which lead to partial passivation of the metal surface and decrease its dissolution rate without preventing electropolymerisation, e.g. [1].

The most investigated conducting polymers for corrosion protection of metals are polyaniline (PANI), polypyrrole (PPy) and their derivatives, e.g. [2–11]. In most of these studies PANI and PPy are electrodeposited on top of the metallic electrodes in an electrolyte solution containing the monomer, which is first used to promote formation of a passive layer and afterwards for electrodeposition of the polymer film.

Polyphenazines are very attractive redox polymers, acting both as conducting polymers and redox mediators, most of their applications being related to their use in sensors and biosensors [12]. In previous work [13,14] the phenazine monomers neutral red (NR), brilliant cresyl blue (BCB), Nile blue A (NB) and safranine T (ST) were electropolymerised on the top of copper electrodes previously passivated in oxalate, hydrogen carbonate and salicylate containing solutions. The success of the electropolymerisation depends not only on the monomer but also on the pre-passivation step, that influences the composition of the passive layer [15,16]. The anti-corrosion behaviour of the films was investigated in 0.10 M KCl using open circuit potential measurements, Tafel plots and electrochemical impedance spectroscopy. It was deduced that PNB improves the corrosion behaviour of copper electrodes, more than the other polyphenazines. PNB films on the top of copper pre-passivated in hydrogen carbonate solution had the highest protection efficiency, ~83%, calculated from Tafel plots after 4 h of immersion in 0.1 M KCl and the highest charge transfer resistance after 72 h of immersion, 27.1 kΩ cm^2 from electrochemical impedance measurements.

Since the properties of conducting polymers are strongly dependent on their morphology and structure [17], in this work scanning electron microscopy was used to examine the morphology of the polyphenazine films formed on copper electrodes. The morphology of the films with the best anti-corrosion behaviour as well as the films with the worst anti-corrosion behaviour were also analysed after 4 h and 72 h immersion in 0.1 M KCl. The mechanism of inhibition obtained from the PNB and PNR films is also discussed.

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* Corresponding author. Tel.: +351 239854470; fax: +351 239827703.
E-mail address: cbrett@ci.uc.pt (C.M.A. Brett).

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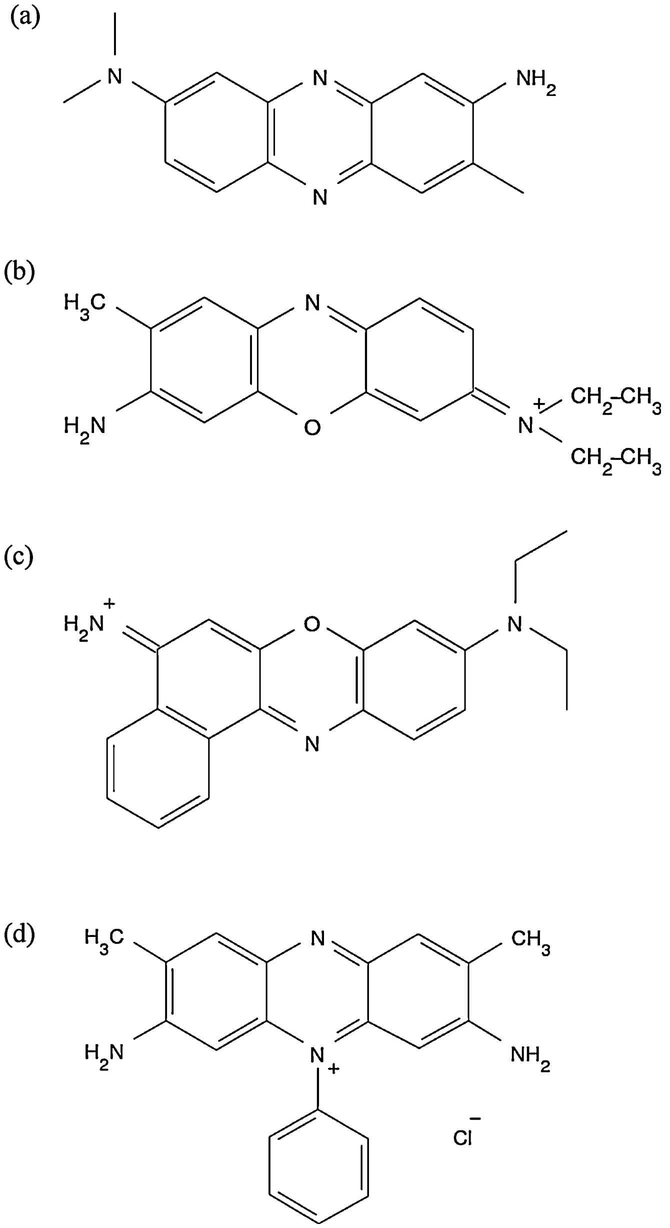

Fig. 1. Chemical structures of phenazine monomers.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals were of analytical reagent grade. The electrolyte solutions used for passivation of copper were 0.125 M sodium oxalate pH 6.85 ($Na_2C_2O_4$, Merck), 0.10 M sodium hydrogen carbonate pH 8.35 ($NaHCO_3$, Riedel-de Haën, Germany), and 0.10 M sodium salicylate pH 6.50 ($NaC_7H_5O_4$, Sigma–Aldrich), concentrations optimised in previous studies. The corrosion behaviour of the modified electrodes was carried out in 0.1 M potassium chloride (KCl, Fluka).

The phenazine monomers, chemical structures shown in Fig. 1, were neutral red (NR) from Aldrich, Germany; brilliant cresyl blue (BCB) from Fluka, USA; Nile blue A (NB) from Fluka, France and Safranine T (ST) was obtained from La Chema, Czech Republic.

The correct amounts of the monomers were dissolved in the supporting electrolytes to give solutions as follows:

- 10 mM NR or 0.5 mM ST in 0.025 M potassium phosphate buffer (KPB) pH 5.54 prepared from di-potassium hydrogen phosphate trihydrate ($K_2HPO_4{\cdot}3H_2O$, Panreac, Spain) and potassium dihydrogen phosphate (KH_2PO_4, Riedel-de Haën, Germany);
- 0.5 mM BCB or 0.5 mM NB in 0.10 M sodium phosphate buffer (NaPB) pH 8.2 prepared from di-sodium hydrogen phosphate dihydrate ($Na_2HPO_4{\cdot}2H_2O$, Fluka, Germany) and sodium dihydrogen phosphate hydrate ($NaH_2PO_4{\cdot}H_2O$, Riedel-de Haën, Germany).

Millipore Milli-Q nanopure water (resistivity > 18 MΩ cm) was used for the preparation of all solutions. All experiments were performed at 24 ± 1 °C.

2.2. Instrumentation

Working electrodes were made from copper cylinders (99.99% purity, Goodfellow Metals, Cambridge, UK) by sheathing in glass and epoxy resin. The exposed disc electrode surface area was 0.20 cm^2. Before experiments, the electrodes were mechanically abraded with 400, 600, 800 and 1500 grade silicon carbide papers. After this procedure, the electrodes were rinsed with water. A platinum foil was used as counter electrode and a saturated calomel electrode (SCE) as reference in a three-electrode cell.

Cyclic voltammetry was performed using a potentiostat/galvanostat Autolab PGSTAT30 connected to a computer with general purpose electrochemical system software (GPES V4.9) from Metrohm-Autolab (Utrecht, Netherlands).

Electrochemical impedance measurements were done with a PC-controlled Solartron 1250 frequency response analyzer, coupled to a Solartron 1286 electrochemical interface using ZPlot 2.4 software (Solartron Analytical, UK). A sinusoidal voltage perturbation of amplitude 10 mV rms was applied in the frequency range between 65 kHz and 0.1 Hz with 10 frequency steps per decade.

Microscope images were acquired using a scanning electron microscope (SEM) JEOL JSM-5310 (JEOL, Tokyo, Japan), equipped with a thermionic field emission SEM and an electronically controlled automatic gun. The images were captured at 10 kV and 20 kV.

2.3. Electrode modification

Copper electrodes were partially passivated by potential cycling in sodium oxalate, salicylate or hydrogen carbonate solutions by potential cycling for 5 cycles at a scan rate of 20 mV s^{-1} in the ranges −0.5 V to +1.0 V with 0.125 M sodium oxalate, −1.0 V to +0.75 V with 0.10 M sodium hydrogen carbonate and −1.2 V to +1.5 V vs SCE with 0.10 M sodium salicylate. The passivated electrodes will be referred to as Cu/oxalate or Cu/$Na_2C_2O_4$, Cu/hydrogen carbonate or Cu/$NaHCO_3$, and Cu/salicylate.

After passivation of the copper electrodes, the phenazine films were prepared by potential scanning from solutions containing the respective monomer. The potential range depends on the electrolyte as well as on the monomer and was:

- PNR film: from −1.5 V to +1.0 V for electrodes passivated in sodium oxalate, −1.0 V to +0.25 V for electrodes passivated in sodium hydrogen carbonate and −1.2 V to +1.5 V for electrodes passivated in sodium salicylate, during 15 cycles at a scan rate of 20 mV s^{-1}.
- PBCB and PNB films: from −1.0 V to +0.5 V for electrodes passivated in sodium oxalate and −1.0 V to +0.75 V for electrodes passivated in sodium hydrogen carbonate, during 20 cycles at a scan rate of 20 mV s^{-1}.
- PST film: from −0.8 V to +0.5 V for electrodes passivated in sodium oxalate and −0.6 V to +0.3 V vs SCE for electrodes passivated in

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