Corrosion Behavior of Hybrid Xerogel Coating Based on Charged Bis-silane Group for Copper substrate

Denise S. Azambuja[a], Débora S. F. Gay[b], Sílvia M. Tamborim[c], Geraldo B. Machado[a], Tânia M. H. Costa[a], Edilson V. Benvenutti[a]
[a]Chemistry Institute, Federal University of Rio Grande do Sul, Av. Bento Gonçalves 9500/91501-970 Porto Alegre, Rio Grande do Sul, Brazil
[b]Federal University of Pampa, Travessa 45, 1650/ 96413-170 Bagé, Rio Grande do Sul, Brazil
[c]Technology Center of Alegrete, Federal University of Pampa, Av. Tiaraju, 810/ 97546-550 Alegrete, Rio Grande do Sul, Brazil
email: denise@iq.ufrgs.br

Introduction

The copper corrosion mechanism in sulfate solutions shows that the conversion of copper metal to cupric and cuprous oxide forms a film on the metal according the following reactions [1].

$4\ Cu + SO_4^{-2} + 6\ H_2O \rightarrow Cu(SO_4)\ .\ 3(OH)_2 + 6\ H^+ + 8\ e^-$

$2\ Cu_2O + SO_4^{-2} + 4\ H_2O \rightarrow Cu(SO_4)\ .\ 3Cu\ (OH)_2 + 2\ H^+ + 4\ e^-$

In order to improve the protective properties of the silane layers on metal surface, the addition of corrosion inhibitors inside the silane film have been made. Among them, surfactants such as cetyltrimethyl ammonium bromide [2], dodecyl sulfate were also added to these films. These surfactants allow an increase on copper corrosion resistance and promote the formation of non-ordered films containing the surfactant and composite molecules. A new charged silica based hybrid material containing the dabco group was synthesized showing thermal stability, water solubility and ability to form films over metal and metal oxide surfaces [3]. This work presents a study of the corrosion protective performance of this novel silica based material containing the 1,4-diazoniabicyclo[2.2.2]octane chloride on copper surface by using EIS and SEM techniques. The effect of cetiltrimethylamonium bromide (CTAB) addition to the hybrid system was evaluated aiming to improve the anticorrosive properties of the coating.

Experimental

Firstly, 8 mmol of the 1,4-diazabicycle[2.2.2]octane (dabco), was dissolved in 20 ml dimethylformamide (DMF), subsequently, 16 mmol of 3-chloropropyltrimethoxy-silane (CPTMS) were added. In this step the cetiltrimethylamonium bromide (CTAB) surfactant (1 and 4 mmol) can be inserted. The mixture was stirred for 72 h, under argon atmosphere at 70 ºC. The white solid obtained was filtered and washed with methyl alcohol and then dried at 70 ºC for 2 h. This resulting solid, 1,4-bis-(3-trimethoxysilypropyl)diazoniabicyclo[2.2.2]octane chloride containing a double charged group, was designated as $(R_2dabco)Cl_2$, and the silane containing the CTAB was assigned $(R_2dabco)Cl_2$/CTAB-1 and $(R_2dabco)Cl_2$/CTAB-4, for 1 and 4 mmol of surfactant added, respectively. These precursors were used for synthesis of silica based hybrid xerogels. Subsequently it was added 7 ml of ethanol, 3.1 or 2.5 ml of tetraethylorthosilicate (TEOS) and 0.3 ml of water under stirring. The resulting hybrid xerogel was called D25 and D40, when it was added 3.1 or 2.5 mL of TEOS, respectively, since these numbers are related to the $(R_2dabco)Cl_2$ molar percentage of 25 and 40 %, i.e. 75 and 60 % of TEOS molar percentage. The synthesis of hybrid xerogel D25 containing $(R_2dabco)Cl_2$/CTAB-1 was made following the same procedure described above and it was designated as D25-1. As well as the hybrid xerogel D40 containing $(R_2dabco)Cl_2$/CTAB-4 was called D40-4. The copper plates (99.99 %) were prepared by grinding with silicon carbide paper up to #1200 grade followed by washing with distilled water and ethanol and dried in a hot air flux . After, they were submitted to pre-treatment with 0.5 mol.l^{-1}NaOH solution, during 3 min. The deposition procedure consisted in the immersion of the metallic sample in the hybrid xerogels at 40 ^{o}C during 30 min and then the panels were cured in an oven at 60 ^{o}C for 60 min. The EIS measurements were performed using an AUTOLAB PGSTAT 30/FRA 2 system. EIS measurements were performed in the potentiostatic mode at OCP. The amplitude of the EIS perturbation signal was 10 mV, and the frequency ranged from 10^5 to 10^{-2} Hz. The test solution was 0.1 mol L^{-1} Na_2SO_4 . SEM images were made in Jeol apparatus JSM 5800 Model using 5 – 20 kV.

Results and Discussion

SEM images of hybrid xerogels containing 1 mol CTAB (D25-1) and 4 mol (D40-4) samples are presented in Figure 1. It is possible to observe that, although there are different amounts of organic content and CTAB, the images were similar and compact.

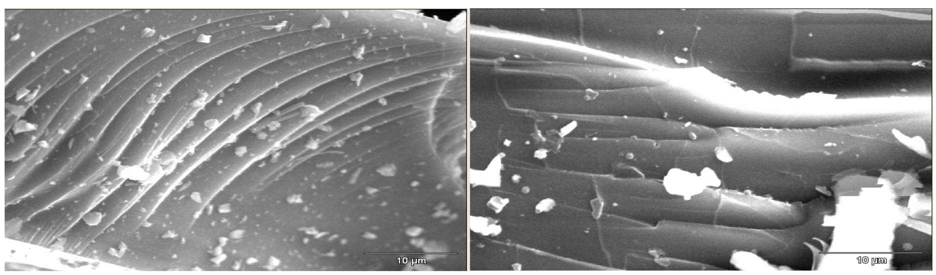

Figure 1: SEM images D25-1 (A) and D40-4 (B)

Previous experiments were performed in order to evaluate the effect of an alkaline pre-treatment of the Cu surface (data not given here). Based on the obtained results the Cu surface was immersed in a 0.1 mol L^{-1} NaOH solution during 1 min. in order to favor the silane deposition. The effect of adding CTAB to the hybrid xerogel was given in Figure 1. The sample treated with no containing surfactant xerogel (D25) shows a diagram with two well defined time constants, being both phase angle near to -50° characteristic of a porous film, presenting a poor corrosion resistance. The Bode diagrams for D25-1 film (with 1 mmol CTAB) shows a maximum phase angle close to -75° indicating an improve of the capacitive character comparatively to the nom-modified xerogel. A decay of the maximum phase angle to -50° and a decrease of the corrosion resistance was detected for films with 4 mmol of CTAB (D40-4) accounting for the formation of a more defective film with an increased number of conductive pathways. Probably the higher CTAB concentration destabilizes the silica network.

Taking into account the best performance of the D25-1 film, it was elected to be used in this work. Different films were made with this xerogel with one, two and three steps depositions (data not shown). The evaluation of the EIS response with immersion time reveals that the film produced by one step deposition shows improved protective character.

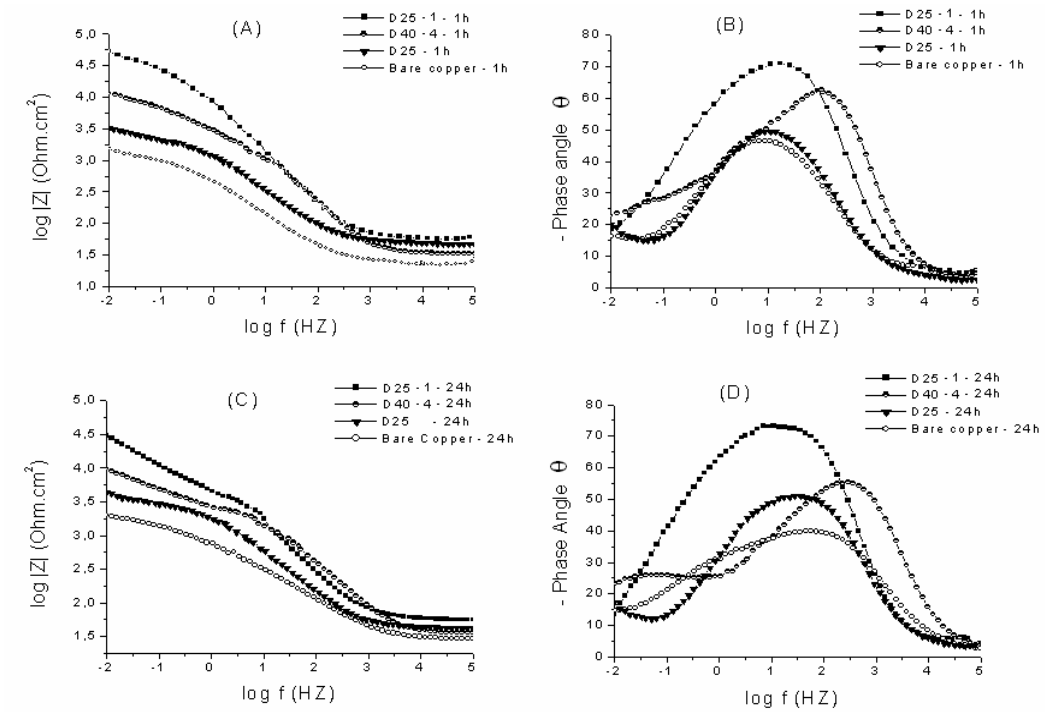

Figure 1: Bode plots for bare copper, copper coated with D25, D25-1 and D40-4 xerogel film in $0.1 molL^{-1}$ Na_2SO_4 solution, at different immersion times: (A) 1h and (B) 24h.

Top view and cross-section images of copper surface coated with D25-1 (data not given here) reveal that the film is relatively homogeneous and have a thickness close to 5 µm.

Conclusions

A novel silica hybrid xerogel containing the double charged 1,4-(silylpropyl)diazoniabicycle[2.2.2]octane chloride group dispersed in cetiltrimethylamonium bromide (CTAB) surfactant was attained. Coating the Cu sample with these novel hybrid xerogel and incorporating an optimal concentration of CTAB (1 mmol) decreases the corrosion rate of the metallic substrate relative to the non-modified hybrid xerogel film.

Acknowledgements

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