Study of Cerium-modified Triazinedithiol Electrodeposited Nanofilm on Corrosion Protection for Aluminum Alloy

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Abstract
The cerium-modified polymeric nanofilm of 6-(N,N-dibutyl)amino-1,3,5-triazine-2,4-dithiol monosodium (DBN) was fabricated by two-step potential electrodeposition onto aluminum alloy for corrosion protection. The structure, surface wettability and corrosion protection of the polymeric nanofilm were investigated by means of fourier transform infrared spectroscopy (FT-IR), water contact angle (WCA), open-circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), respectively. FT-IR result revealed that DBN monomer had successfully been polymerized on aluminum alloy surface by electrochemical deposition in the absence and presence of cerium and the addition of cerium had no influence on FT-IR of the polymeric nanofilm. The result of surface wettability showed that WCA of aluminum alloy cerium-modified polymeric nanofilm was slightly higher compared with that without cerium. Electrochemical measurements demonstrated that the cerium-modified polymeric nanofilm on aluminum alloy surface exhibited remarkable corrosion protection property, which could be ascribed to the precipitation of cerium oxides or hydroxides on aluminum surface or the coordination between cerium and heterocyclic π-electron in polymeric nanofilm to prevent corrosive particles to the surface of aluminum substrates.

Keywords: Aluminum alloy; Cerium-modified; Electrodeposition; Polymeric nanofilm; Corrosion protection

Introduction
Due to good adhesion, anti-corrosion, superhydrophobicity, lubrication and dielectric property on a variety of metal substrates, the application of triazinedithiol compounds has attracted many researchers’ attention during the past decade [1-11]. Especially, as the anti-corrosion materials, the triazinedithiol polymeric nanofilm exhibits basic corrosion resistance [12]. Unfortunately, the polymeric nanofilms fabricated by traditional techniques [4,7-9,13] have the propensity for containing molecule-sized defects to some extent, which limits its application in more fields. In order to reduce the defects in the polymeric nanofilm, some other methods have been extensively studied in the past few years, such as the change of the substituent on triazinedithiol’s structure [12], the combination of self-assembled method and electrodeposition [10] as well as the preparation of complex nanofilm [11]. These techniques enhanced the anti-corrosion property for metals to some degree.

It is well known that cerium ion as corrosion inhibitor doped in nanofilm can inhibit the corrosion of metal substrates and improve anti-corrosion property because of its self-healing ability [14-17]. Although the mechanism is not fully clear, some publications are still reported using cerium such as Ce(NO$_3$)$_3$, to enhance the corrosion resistance of the nanofilms [18,19]. However, the techniques mentioned above to dope foreign cerium components mostly focused on utilizing silane agents as matrix to prepare functional films. As a promising environmentally coating, it has not been reported so far to dope cerium into the triazinedithiol polymeric nanofilm. It is known that triazinedithiol compounds have triazine ring which presents electronegativity, while cerium shows electropositivity. It could be assumed that triazine ring and cerium might combine with each other by a weak electrostatic force or coordinative bond during the electrodeposited process to obtain the denser hybrid nanofilm. When the metal corrosion occurred, cerium might come out to product the precipitation of cerium hydroxides or cerium oxides to protect the substrate in the vicinity of the cathodic sites, where OH$^-$ ions were formed from the oxygen reduction reaction. Therefore, incorporating cerium into triazinedithiol nanofilm is believed to enhance anti-corrosion performance.

In this paper, we chose AA5052 aluminum alloy as substrate and 6-(N,N-dibutyl)amino-1,3,5-triazine-2,4-dithiol monosodium (DBN) as triazinedithiol monomer to fabricate the polymeric nanofilm of DBN with the aid of electrochemical technique. Meanwhile, Ce(NO$_3$)$_3$ as inhibitor was adopted to prepare cerium-doped polymeric nanofilm by two-step potential electrodeposition. The structure and surface wettability of those polymeric nanofilms were studied by fourier transform infrared spectroscopy (FT-IR) and water contact angle measurements (WCA). The corrosion resistance of those nanofilms on aluminum alloy were investigated by open-circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

Experimental
Materials and reagents
The substrate for this study was AA5052 aluminum alloy with the dimension of 30 mm × 50 mm × 0.3 mm and the chemical compositions of AA5052 were shown in Table 1. All test plates were ultrasonically cleaned and dried in a vacuum oven.

| Element | Cu | Si | Fe | Mn | Mg | Zn | Cr | other |
|---------|----|----|----|----|----|----|----|-------|
| Mass fraction (%) | 0.1% | 0.2% | 0.4% | 0.1% | 2.8% | 0.1% | 0.3% | 0.15% |

Table 1: Chemical composition for aluminum alloy AA5052 (mass fraction).

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degassed with acetone for 15 min and blow-dried with warm air, followed by corona treatment (50 V, 2.0 A) for 20 s. DBN monomer was synthesized by the reaction of 1,3,5-triazine-2,4,6-trichloride with dibutyl amine and NaSH, according to the method described in the previous paper [20]. The molecular structure of DBN was shown in Figure 1. All of the chemicals were employed as analytical reagents without further purification. Distilled water was used as solvent and NaNO2 was applied as supporting electrolyte for electrodeposition. Cerium nitrate (Ce(NO3)3, purity ≥ 99.0%) was used as adding component to modify electrodeposited nanofilm. The concentrations of DBN, NaNO2 and Ce(NO3)3 were kept constant at 5 mM, 0.15 M and 0.5 mM, respectively.

### Preparation of electrodeposited polymeric nanofilm

The electrodeposition was performed by using a three-electrode cell, with the AA5052 alloy plate as a working electrode, the saturated calomel electrode (SCE) as a reference electrode and the stainless steel plate as counter electrode. The electrodeposited polymeric nanofilm of DBN was prepared by two-step potentiostat method using electrochemical workstation (CHI 660C, CH Instrument, Shanghai, China) on AA5052 surface. The first step potential was 1.6 V and 6.0 V was applied for the second step. Electrodeposition time corresponded to two-step potential was 30 s and 10 s, respectively. After the electropolymerization, the samples were taken out from the electrolytic cell and immediately rinsed by distilled water and acetone, then blow-dried with warm air. Finally, the samples were cured at 100°C for 10 min in an oven.

### Characterization of electrodeposited nanofilm

FT-IR was carried out by attenuated total reflection spectroscopy (Bruker TENSOR 37) in the range of 4,000 to 600 cm⁻¹. WCA was measured by optical contact angle measuring instrument (SL100) at room temperature with 2 μL distilled water. OCP was performed for 1200 s by electrochemical workstation in 0.5 M sodium chloride (NaCl) aqueous solution. Potentiodynamic polarization were conducted from -0.9 V to -0.1 V with the scanning rate of 0.5 mV/s in 0.5 M NaCl aqueous solution for pitting corrosion study or in 1 M H2SO4 solution for uniform corrosion study, respectively. EIS was recorded over a frequency range from 10 mHz to 100 kHz with the excitation voltage of 10 mV after 1 hour immersion time in 0.1 M NaCl solution under open-circuit potential.

### Results and Discussion

#### FT-IR spectra analysis

FT-IR spectra measurements were conducted by reflection absorption and potassium bromide (KBr) method to investigate the change of chemical structure from monomer (a) to polymeric nanofilm (b) of DBN as showed in Figure 2. In Figure 2a, the presence of triazine ring was confirmed by the absorption peaks at 1564 cm⁻¹, 1536 cm⁻¹ and 1465 cm⁻¹ >C=N- bonds and the absorption peaks at 1375 cm⁻¹ and 1331 cm⁻¹ due to C-N bonds. Dibutyl amino groups were confirmed by the absorption peaks at 2959 cm⁻¹ and 2931 cm⁻¹ due to C-H symmetric stretching vibrations of -CH₂ and -CH₃ and the absorption peak at 2868 cm⁻¹ due to C-H asymmetric stretching vibrations of -CH₃. Meanwhile, the peaks at 3410 cm⁻¹ and 3161 cm⁻¹ were clearly detected, which were assigned to the stretching vibration of N-H. After electrochemical polymerization (Figure 2b), the absence of peak at 3410 cm⁻¹ and 3161 cm⁻¹ and the presence of a new broaden strong absorption peak at 926 cm⁻¹ were observed, which could ascribe to the formation of S-Al or O-Al on AA5052 surface. However, for the cerium modified polymeric nanofilm, FT-IR spectroscopy did not give any obvious difference in the structure (data not shown), suggesting that the addition of cerium did not influence the production of polymeric nanofilm. The above results revealed that polymeric nanofilms were formed on AA5052 substrate surface by electropolymerization of DBN no matter whether cerium was added or not.

#### Contact angle measurement

WCA were usually used to characterize the wettability of material surface. To confirm the formation of polymeric nanofilms in the absence and presence of cerium, WCA of aluminum surface was measured before and after the formation of nanofilms as shown in Figure 3. WCA of the blank aluminum alloy surface was 91.5°, while WCA of the blank substrate after corona discharge treatment sharply dropped to 14.4°, suggesting that the pretreated blank aluminum alloy had been converted into a hydrophilic substrate from a weak hydrophobic substrate. It can be attributed to the destruction of natural oxidation film on aluminum.
alloy surface and the formation of hydrophilic group after corona discharge treatment. For the electrodeposited nanofilm of DBN in the absence of cerium, WCA increased to 109.3° and was up to 111.4° for the electrodeposited nanofilm in the presence of cerium. These results demonstrated that DBN monomers were electropolymorized on aluminum substrate surface to form the polymeric nanofilms, which resulted in the improvement of the hydrophobicity of the surface. Furthermore, the electrodeposited polymeric nanofilm modified by cerium (III) had slightly higher hydrophobicity. Humid environment is one reason of aluminum alloy corrosion, and the hydrophobic surface of substrate is benefit for the protection of aluminum alloy [11]. It was proposed that electrodeposited polymeric nanofilms in the absence or presence of cerium could have excellent protective effect for substrate surface.

Open-circuit potential (OCP)

Figure 4 displayed a comparison of the OCP of blank, electrodeposited polymeric nanofilm covered the substrate surfaces in the absence and presence of cerium (III) in 0.5 M NaCl solution for 1200 s. For the corrosion system, the OCP and the corrosion potential were the basic problem for the corrosion phenomena. In general, the more negative the OCP, the better the cathodic protection effect. The potential measurement clearly demonstrated a negative shift in OCP for AA5052 covered by electrodeposited polymeric nanofilms in the absence and presence of cerium (III). This behavior could be attributed to protective effect of the electrodeposited polymeric nanofilms on the aluminum surface that slowed down the cathodic reaction of substrate. Furthermore, OCP of the electrode covered by cerium-doped polymeric nanofilm was more negative than that without cerium-doped nanofilm, clearly suggesting the cathodic protection effect of cerium component.

Potentiodynamic polarization

To study the resistance to pitting corrosion of these electrodeposited nanofilms for aluminum alloy surface, the potentiodynamic polarization test was performed in 0.5 M NaCl aqueous solution as shown in Figure 5. The electrochemical parameters such as corrosion potential (E\text{corr}), corrosion current density (I\text{corr}), and anodic/cathodic tafel slopes (β\text{a} and β\text{c}) which were determined by the tafel extrapolation method, were presented in Table 2. According to the approximate linear polarization, the corrosion potential (E\text{corr}), polarization resistance (R\text{p}) and protection efficiency (PE) could be obtained by the following expressions [21,22].

$$R_p = \beta_\text{c}/2.3 \times I_\text{corr}$$

$$PE = (1 - I_\text{corr}/I_\text{corr}^0) \times 100\%$$

where I\text{corr} and I\text{corr}^0 were the corrosion current densities of AA5052 covered by polymeric nanofilms and blank, respectively.

From Figure 5 and Table 2, it was seen that the corrosion potentials of blank and electrodeposited polymeric nanofilms modified AA5052 electrodes in the absence and presence of cerium (III) were -0.620 V, -0.418 V and -0.485 V, respectively. The corrosion current density (I\text{corr}) decreased from 1.21×10^{-3} A/cm² for blank electrode to 8.73×10^{-5} A/cm² for electrodeposited polymeric nanofilms covered AA5052 without cerium (III). As for cerium-doped polymeric nanofilm covered AA5052 electrode, the I\text{corr} dropped to 5.54×10^{-5} A/cm², suggesting that cerium-doped polymeric nanofilm exhibited more favorable inhibition performance. It is assumed that the precipitation of cerium hydroxide or oxide was produced in the vicinity of the cathodic sites, where OH ions were formed from the oxygen reduction reaction. The protection efficiencies calculated by the expression (2) were determined to be as high as 92.7% for none cerium-doped polymeric nanofilm, while it was up to 95.5% for cerium-doped polymeric nanofilm. The result demonstrated that the active corrosion inhibition effect of cerium incorporated into the polymeric nanofilm exhibited an improvement for the protectiveness of AA5052.

To further investigate the resistance to uniform corrosion of these electrodeposited nanofilms for aluminum alloy surface, the potentiodynamic polarization was conducted in 1.0 M H\text{2}SO\text{4} solution as displayed in Figure 6. The electrochemical parameters of E\text{corr}, I\text{corr} and β\text{c} and β\text{a} are given in Table 3 according to the same method mentioned above. The polarization resistance and protection efficiency were also
calculated by the above expression (1) and expression (2).

It can be noted that the $E_{corr}$ of blank, and electrodeposited polymeric nanofilms modified AA5052 electrodes in the absence and presence of cerium (III) were -0.467 V, -0.483 V, and -0.474 V, respectively. $I_{corr}$ of electrodeposited polymeric nanofilm covered AA5052 electrode reduced two orders of magnitude than that of blank electrode. Similarly, $I_{corr}$ decreased from $9.11 \times 10^{-7}$ A/cm$^2$ for electrodeposited polymeric nanofilm covered AA5052 in the absence of cerium (III) to $6.70 \times 10^{-7}$ A/cm$^2$ for cerium-doped polymeric nanofilm covered AA5052 electrode. The protection efficiency of polymeric nanofilm in the absence of cerium (III) for AA5052 was 92.5%, while 94.5% for cerium-doped polymeric nanofilm coated surface, which was consistent with the result of pitting corrosion. The shift of $E_{corr}$ to negative direction and decrease of $I_{corr}$ demonstrated that the corrosion of AA5052 surface was considerably suppressed by the covering of electrodeposited polymeric nanofilm, and the cerium-doped polymeric nanofilm covered AA5052 exhibited more excellent anticorrosion property than that without cerium. It can be inferred that the coordination between cerium and heterocyclic π-electron in polymeric nanofilm to prevent corrosive particles to the substrate surface to make corrosion protection of the cerium-doped polymeric nanofilm be improved.

**EIS analysis**

In order to estimate the anti-corrosion performance of these polymeric nanofilms, EIS was also employed. Figure 7 presented the bold plot of blank, electrodeposited polymeric nanofilm covered AA5052 electrodes in the absence and presence of cerium (III). It can be seen that the impedance modulus values of polymeric nanofilms covered substrate were higher than that of blank over the frequency range, which demonstrated polymeric coatings could provide corrosion protection for aluminum alloy substrate. Especially in low frequency range, the impedance modulus value of cerium-modified polymeric nanofilm was an order of magnitude higher than that without cerium and two orders of magnitude higher than blank. Generally, phase angle was rather related to the nanofilm characteristics and anti-corrosion property of substrate and the higher phase angle implied good uniform corrosion resistance. For cerium-doped polymeric nanofilm, the phase angle was always approaching to -90° in a wide range of frequency and its phase shifts reduced less than that of blank and electrodeposited polymeric nanofilm in the absence of cerium from medium to low frequency, which also indicated that the stability of the cerium-doped nanofilm was improved.

Meanwhile, the impedance could be evaluated by the radius of the capacitive loops in Nyquist plots as shown in Figure 8. It was found that no matter whether cerium or not, polymeric nanofilms covered substrate surface had significantly higher impedance than blank.
Moreover, compared with electrodeposited polymeric nanofilm in the absence of cerium, the cerium-modified nanofilm presented larger capacitive loops, which meant that cerium-modified nanofilm had more effective anti-corrosion property. The EIS result was consistent with the $R_{\text{ct}}$ value of potentiodynamic polarization.

In order to explain the mechanism of corrosion protection, EIS results could be numerical fitted by equivalent circuit. Figure 9 displayed the model of EIS spectra. $R_0$ was the simulation of the solution resistance, the constant phase element (CPE1) was responsible for the film capacitance and $R_1$ accounted for polarization resistance, respectively. The values of $R_0$, $R_1$, and total capacitance ($T$) of the CPE1 were calculated by fitting the experimental data using ZView software as listed in Table 4. The $R_0$ value was significantly relied on the property of these polymeric nanofilms and intensely dependent on anti-corrosion performance of the nanofilms. So the higher $R_0$ value represented good uniform anti-corrosion performance. It was clearly observed that the $R_0$ value of cerium-modified polymeric nanofilm was the highest, implying that the film was the most compact and the corrosion resistance of electrodeposited polymeric nanofilm of DBN could be improved by doping a certain amount of cerium. On the basis of the above results, it could be assumed that cerium as corrosion inhibitor did enhance anti-corrosion performance of electrodeposited polymeric nanofilm of DBN.

### Table 4: EIS parameters by fitting the experimental data. (a) blank; (b) electrodeposited polymeric nanofilm covered AA5052 without cerium (iii); (c) electrodeposited polymeric nanofilm covered AA5052 with cerium (iii).

| Sample | $R_0$ (Ω·cm$^2$) | CPE1-T (F/cm$^2$·s$^n$) | CPE1-P | $R_1$ (Ω·cm$^2$) |
|--------|------------------|-------------------------|---------|------------------|
| (a)    | 6.403            | 4.75×10$^4$             | 0.8737  | 1.405×10$^5$    |
| (b)    | 1.883            | 1.57×10$^4$             | 0.84512 | 1.173×10$^4$    |
| (c)    | 0.989            | 7.74×10$^2$             | 0.86545 | 3.392×10$^1$    |

### Conclusion

The cerium-modified polymeric nanofilm of DBN was successfully prepared by two-step potential electrodeposition onto AA5052 substrate surface. WCA of aluminum alloy surface covered by cerium-modified polymeric nanofilm was higher, which exhibited a certain hydrophobicity. The electrochemical measurements of OCP, potentiodynamic polarization and EIS demonstrated that the substrate surface covered by cerium-doped polymeric nanofilm had remarkable anti-corrosion property. Cerium as corrosion inhibitor does improve the corrosion resistance of polymeric nanofilm and further studies are necessary to fully understand the mechanism of Ce(NO$_3$)$_3$.

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