

CORROSION INHIBITION OF CARBON STEEL BY LDH/GO HYBRID INTERCALATED WITH 2-BENZOTHAZOLYTHIO-SUCCINIC ACID

**Nguyen Thuy Duong¹, Tran Boi An², Phan Thanh Thao², Nguyen Anh Son¹,
Vu Ke Oanh¹, Trinh Anh Truc¹, To Thi Xuan Hang^{1*}**

¹*Institute for Tropical Technology, Vietnam Academy of Science and Technology
18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam*

²*Institute of Chemical Technology, Vietnam Academy of Science and Technology
1 Mac Dinh Chi, District 1, Ho Chi Minh City*

*Email: ttxhang60@gmail.com

Received: 30 August 2017; Accepted for publication: 6 October 2017

ABSTRACT

Layered double hydroxide/graphene oxide hybrid (LDH/GO) intercalated with corrosion inhibitor 2-benzothiazolylthio-succinic acid (BTSA) was prepared using co-precipitation method. The synthesized LDH/GO-BTSA was characterized by FTIR, XRD and SEM. The inhibitive action of LDH/GO-BTSA on carbon steel was evaluated and compared with LDH-BTSA by electrochemical measurement. It was shown that the GO and BTSA were intercalated in LDH structure. The obtained results showed that LDH/GO-BTSA is anodic corrosion inhibitors, and the inhibition efficiency was 94 % at concentration of 1 g/l.

Keywords: layered double hydroxide, graphene oxide, corrosion inhibitor, carbon steel.

1. INTRODUCTION

Layered double hydroxides (LDHs) are known as anionic clays. They are composed of positively charged hydroxide layers similar to the brucite structure with intercalated anions and water molecules between the layers. LDHs with anion-exchange capability have been investigated as a container of corrosion inhibitors for corrosion protection of metals [1-6]. The corrosion inhibitors can be released from the LDH container by exchange reaction with aggressive anions Cl⁻. The LDH containers have two roles: absorbing the harmful anions and releasing the inhibiting anions [1, 7]. Graphene oxide is usually synthesized from the oxidation of graphite by strong oxidants. Graphene and graphene oxide have the reinforcing effect on mechanical, thermal and barrier properties of organic coatings based on different binders like polyurethane, polyacrylic, epoxy resin [8 - 13]. LDHs and graphene have lamellar structure and complementary properties, and hydrotalcite/graphene composites have been studied for application in different fields [14-16]. For organic coatings the combination of hydrotalcite and graphene has the synergistic effect on the fire retardation of materials [13, 17]. In our previous works, layered double hydroxides intercalated with 2-benzothiazolylthio-succinic acid (BTSA)

as a container of corrosion inhibitor was studied for corrosion protection of carbon steel [18-20]. ZnAl LDH intercalated with BTSA exhibits higher inhibiting performance than BTSA modified MgAl LDH. The presence of BTSA modified LDH improved corrosion protection, resistance to cathodic disbonding and the adhesion of the epoxy coating.

In this work, layered double hydroxide/graphene oxide hybrid intercalated with corrosion inhibitor 2-benzothiazolylthio-succinic acid (LDH/GO-BTSA) was prepared. The synthesized LDH/GO-BTSA was characterized by FTIR, XRD and SEM. The inhibition effect of LDH/GO-BTSA on carbon steel was evaluated and compared with LDH-BTSA by polarisation curves and electrochemical impedance spectroscopy.

2. EXPERIMENTAL

2.1. Materials

Sodium hydroxide, zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$, aluminum nitrate nonahydrate $Al(NO_3)_3 \cdot 9H_2O$, $Na_2MoO_4 \cdot 2H_2O$ were purchased from Merck. Corrosion inhibitor, 2-benzothiazolylthio-succinic acid (BTSA) was obtained from Ciba Company.

2.2. Preparation of graphene oxide

Natural graphite was expanded in supercritical CO_2 environment at 50 °C, pressure of 15 MPa. Graphene oxide was synthesized from expanded graphite powder by modified Hummer's method. 2.0 g of the expanded graphite and 7 g of $KMnO_4$ were gradually added into 50 mL concentrated H_2SO_4 at 2 °C. Then the temperature of the mixture was increased to 35 °C and kept for 2 hours. After that 300 mL distilled water was added in the mixture, stirred for 1 hours, then 10 mL 30 % H_2O_2 was added to the mixture. The precipitate was filtered, washed with distilled water and dried in vacuum at 50 °C for 24 hours.

2.3. Preparation of LDH-BTSA and LDH/GO-BTSA

The layered double hydroxides intercalated with BTSA (LDH-BTSA) were prepared using the co-precipitation method [21]. A mixture metal nitrate solution of 0.125 mol of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.0625 mol of $Al(NO_3)_3 \cdot 9H_2O$ in 125 mL of degassed distilled water was added dropwise to a solution of 0.313 mol of BTSA with the molar equivalent. The pH of the solution was maintained at 8 - 9 by adding 1M NaOH solution. The mixture was stirred under an inert nitrogen atmosphere for 24 h at the temperature of 65°C. Then the sample was washed with large amounts of degassed distilled water by centrifugation before drying at 50 °C in a vacuum oven for 24 h.

The layered double hydroxide/GO hybrid intercalated with BTSA (LDH/GO-BTSA) was synthesized using the procedure described as the preparation of LDH-BTSA except for the solution of 0.313 mol of BTSA containing GO with GO/LDH ratio of 1/20.

2.5. Analytical characterizations

The FTIR spectra of GO, LDH-BTSA and LDH/GO-BTSA were obtained using the KBr method on a Nexus 670 Nicolet spectrometer operated at 1 cm^{-1} resolution in the 400–4000 cm^{-1} region.

Powder X-ray diffraction patterns of GO, LDH-BTSA and LDH/GO-BTSA were taken using a Siemens diffractometer D5000 with CuK_α radiation (1.5406 \AA) at room temperature under air conditions.

The particle size and morphology of LDH-BTSA and LDH/GO-BTSA were determined by field emission scanning electron microscope using Hitachi 4800 equipment.

2.6. Electrochemical characterization

For the electrochemical measurements, a three-electrode cell was used with a platinum auxiliary electrode, a saturated calomel reference electrode (SCE) and a working electrode with an exposed area of 1 cm^2 for the bare carbon steel. Anodic and cathodic polarization curves, in the presence and absence of hydrotalcites, were obtained after 2 h of immersion at a scan rate of 1 mV s^{-1} starting from the corrosion potential. The electrochemical impedance measurements were performed using a VSP 300 Bio-logic by EC-Lab over a frequency range of 100 kHz–10 MHz with six points per decade using 5 mV peak-to-peak sinusoidal voltage. The corrosive medium was prepared from distilled water by adding NaCl (reagent grade); the NaCl solution concentration was 0.1 M.

3. RESULTS AND DISCUSSION

3.1. Characterization of LDH/GO-BTSA

The FT-IR spectra of GO, LDH-BTSA and LDH/GO-BTSA are presented in Fig.1. The FT-IR spectrum of GO presents bands characteristic of C-O and C=O at 1406 cm^{-1} and 1717 cm^{-1} respectively [22]. The Band at 1621 cm^{-1} is attributed to C=C vibration [23]. In the FT-IR spectrum of LDH-BTSA, it is observed the bands characteristic of Zn-O and Al-O at 430 cm^{-1} and 615 cm^{-1} , respectively [24]. The band at 1575 cm^{-1} is attributed to COO^- group [25]. This indicates the presence of BTSA in the form of carboxylate in the LDH-BTSA. The FT-IR spectrum of LDH/GO-BTSA presents the characteristic bands of LDH-BTSA at 427 cm^{-1} , 618 cm^{-1} and 1577 cm^{-1} [25]. The band characteristic of GO at 1618 cm^{-1} is also observed. These results indicate that GO and BTSA are present in LDH structure.

The XRD patterns of GO, LDH-BTSA and LDH/GO-BTSA are shown in the Fig.2. For GO it is observed a strong peak at 11.2° corresponding to interlayer distance of 0.79 nm. This confirms the complete oxidation of graphite to the GO [26]. The XRD pattern of LDH-BTSA shows typical peaks of LDH structure and the (003) reflection corresponding to the basal spacing of 0.82 nm and 1.65 nm which are higher than the one of LDH [27]. The increase of d-spacing values indicates the intercalation of BTSA in the interlayer domain of LDH. For LDH/GO-BTSA, it is observed also the similar diffraction peaks like those of LDH-BTSA and the (003) reflection corresponding to the basal spacing of 0.81 nm and 1.66 nm which are close to the ones of LDH-BTSA. The reflection corresponding to the basal spacing of 0.81 nm is overlapping with characteristic peak of GO.

It can be seen that GO has layer structure with wrinkled large surface. LDH-BTSA presents a typical plate-like morphology of hydrotalcite with the particle size in the range of 50-200 nm. LDH/GO-BTSA has also layer structure with lower crystallinity and particle size in the same order of LDH-BTSA. It is not observed the GO structure in the SEM image of LDH/GO-BTSA. These results can be explained by the formation of LDH-BTSA on GO surface. This result is similar to the results in the literature [28].

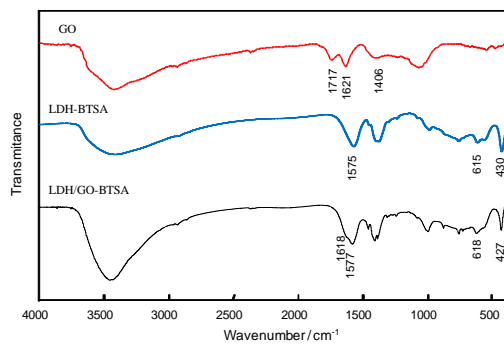


Figure 1. FTIR spectra of GO, LDH-BTSA and LDH/GO-BTSA.

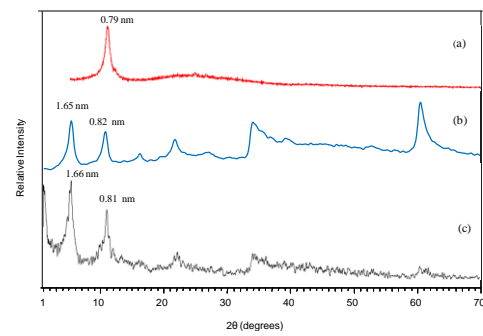


Figure 2. XRD patterns of (a) GO, (b) LDH-BTSA and (c) LDH/GO-BTSA.

SEM images of GO, LDH-BTSA and LDH/GO-BTSA are shown in Fig. 3.

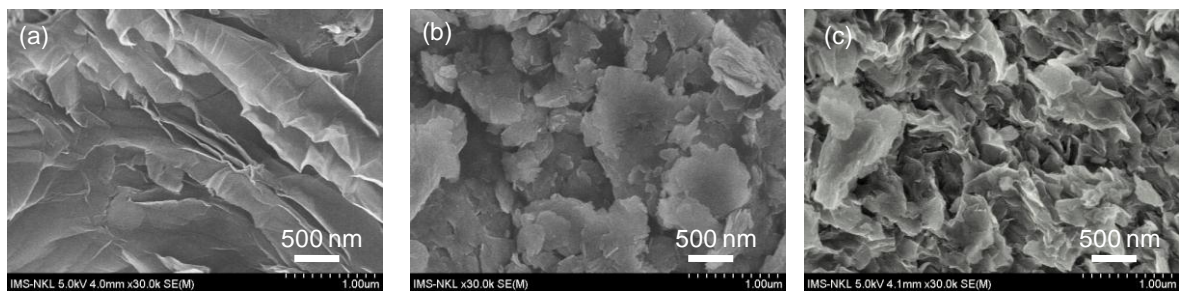


Figure 3. SEM images of (a) GO, (b) LDH-BTSA and (c) LDH/GO-BTSA.

3.2. Corrosion inhibition effect of LDH/GO-BTSA

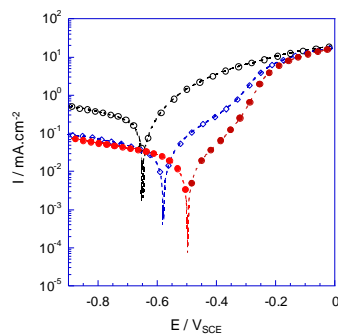


Figure 4. Polarization curves obtained for electrode after 2 h of immersion in 0.1 M NaCl solution (o) without inhibitor, (◊) with 1 g/l LDH-BTSA and (●) with 1 g/l LDH/GO-BTSA.

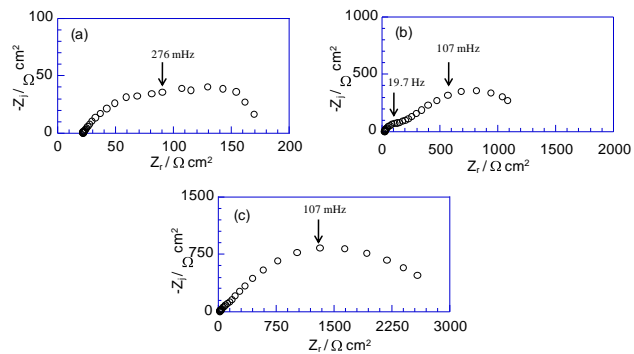


Figure 5. Electrochemical impedance diagrams obtained for electrode after 2 h immersion in 0.1 M NaCl solution (a) without inhibitor, (b) with 1 g/l LDH-BTSA and (c) with 1 g/l LDH/GO-BTSA.

The polarization curves obtained for electrode after 2 h of immersion in 0.1 M NaCl solution without hydrotalcite, with LDH-BTSA and LDH/GO-BTSA at concentration of 1 g/l are presented in Fig. 4. In the presence of LDH-BTSA and LDH/GO-BTSA a shift of the corrosion potential toward more positive values and lower anodic current densities and cathodic current densities can be observed. The corrosion potential obtained with LDH/GO-BTSA is

more positive than this value of LDH-BTSA and the anodic current densities are lower than the one of LDH-BTSA. The polarization curves show that the LDH-BTSA and LDH/GO-BTSA are anodic inhibitors of the carbon steel. Fig. 5 shows the impedance diagrams obtained for the carbon steel electrode after 2 h of immersion in 0.1 M NaCl solution at the corrosion potential without inhibitor and with LDH-BTSA and LDH/GO-BTSA at concentration of 1 g/l.

The value of the polarization resistance can be used to evaluate the inhibition efficiency: $E\% = (R_p - R_{p0})/R_p$, where R_p and R_{p0} are the polarization resistances in the presence and absence of inhibitor, respectively.

The R_{p0} value obtained without inhibitor is about $170 \Omega \cdot \text{cm}^2$. The R_p value obtained in the presence of LDH-BTSA is $1170 \Omega \cdot \text{cm}^2$ and the calculated inhibition efficiency is 85.5 %. The R_p value obtained in the presence of LDH/GO-BTSA is $2960 \Omega \cdot \text{cm}^2$ and the inhibition efficiency is 94.2 %, which is much higher than this value of LDH-BTSA. This result indicates that the presence of GO in LDH/GO-BTSA improved the corrosion inhibition of LDH-BTSA. The Higher corrosion efficiency of LDH/GO-BTSA compared with LDH-BTSA can be explained by the barrier effect of GO in LDH/GO-BTSA.

4. CONCLUSIONS

Layered double hydroxide/graphene oxide hybrid intercalated with corrosion inhibitor 2-benzothiazolythio-succinic acid was successfully synthesized using the coprecipitation method. The polarization curves obtained on carbon steel show that LDH-BTSA and LDH/GO-BTSA are anodic corrosion inhibitors and their efficiencies at the concentration of 1 g/l were 85.5 % and 94.2 %, respectively. The presence of GO improved corrosion inhibition effect of LDH/GO-BTSA.

Acknowledgments. The authors gratefully acknowledge the financial support of Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.01-2016.06.

REFERENCES

1. Mahajanam P. V., Buchheit R. G. - Characterization of Inhibitor Release from Zn-Al-[V10O28]6- Hydrotalcite Pigments and Corrosion Protection from Hydrotalcite-Pigmented Epoxy Coatings, *Corrosion* **64** (2008) 230-240.
2. Zheludkevich M. L., Poznyak S. K., Rodrigues L. M., Raps D., Hack T., Dick L. F., Nunes T., Ferreira M. G. S. - Active protection coatings with layered double hydroxide nanocontainers of corrosion inhibitor, *Corrosion Science* **52** (2010) 602-611.
3. Li D., Wang F., Yu X., Wang J., Liua Q., Yang P., He Y., Wang Y., Zhang M. - Anticorrosion organic coating with layered double hydroxide loaded with corrosion inhibitor of tungstate, *Prog. Org. Coat.* **71** (2011) 302-309.
4. Williams G., McMurray H. N. - Inhibition of Filiform Corrosion on Polymer Coated AA2024-T3 by Hydrotalcite-Like Pigments Incorporating Organic Anions, *Electrochem. Solid-State Lett.* **7** (2004) B13-B15.
5. Poznyak S. K., Tedim J., Rodrigues L. M., Salak A. N., Zheludkevich M. L., Dick L. F. P., Ferreira M. G. S. - Novel Inorganic Host Layered Double Hydroxides Intercalated with

- Guest Organic Inhibitors for Anticorrosion Applications, *Appl. Mater. Interfaces* **1** (2009) 2353–2362.
6. Buchheit. R. G., Guan. H., Mahajanam. S., Wong. F. - Active corrosion protection and corrosion sensing in chromate-free organic coatings, *Prog. Org. Coat.* **47** (2003) 174-182.
 7. Tedim J., Kuznetsova A., Salak A.N., Montemor F., Snihirova D., Pilz M., Zheludkevich M. L., Ferreira M. G. S. - Zn–Al layered double hydroxides as chloride nanotraps in active protective coatings, *Corrosion Science* **55** (2012) 1–4.
 8. Wan Y. J., Tang L. C., Gong L. X., D. Yan, Li Y. B., Wu L. B., J. X. Jiang, Lai G. Q. - Grafting of epoxy chains onto graphene oxide for epoxy composites with improved mechanical and thermal properties, *Carbon* **69** (2014) 467–480.
 9. Tang L. C., Wan Y. J., Yan D., Pei Y. B., Zhao L., Li Y. B., Wu L. B., Jiang J. X., Lai G. Q. - The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites, *Carbon* **60** (2013) 16–27.
 10. Chang K. C., Hsu M. H., Lu H. I., Lai M. C., Liu P. J., Hsu C. H., Ji W. F., Chuang T. L., Wei Y., Yeh J. M., Liu W. R. - Room-temperature cured hydrophobic epoxy/graphene composites as corrosion inhibitor for cold-rolled steel, *Carbon* **66** (2014) 144–153.
 11. Li Z., Wang R., Young R. J., Deng L., Yang F., Hao L., Jiao W., Liu W. - Control of the functionality of graphene oxide for its application in epoxy nanocomposites, *Polymer* **54** (2013) 6437–6446.
 12. Lin J., Zhang P., Zheng C., Wu X., Mao T., Zhu M., Wang H., Feng D., Qian S., Ca X. - Reduced silanized graphene oxide/epoxy-polyurethane composites with enhanced thermal and mechanical properties, *Applied Surface Science* **316** (2014) 114–123.
 13. Hang T. T. X., Truc T. A., Duong N. T., Pébère N., Olivier M. G. - Layered double hydroxides as containers of inhibitors in organic coatings for corrosion protection of carbon steel, *Prog. Org. Coat.* **74** (2011) 343–348.
 14. Wu X.W., Du N., Li H.P., Zhang R.J., Hou W.G. - Synthesis and characterization of camptothecin/graphene oxide/hydrotalcite-like compounds nanohybrids, *Acta Chim. Sinica* **72** (2014) 963–969.
 15. Sunil P. Lonkar¹, Jean-Marie Raquez, Philippe Dubois - One-Pot Microwave-Assisted Synthesis of Graphene/Layered Double Hydroxide (LDH) Nanohybrids, *Nano-Micro Lett.* **7**(4) (2015) 332–340
 16. Yayun Zhong, Yuqing Liao, Aimei Gao, Junnan Hao, Dong Shu, Yulan Huang, Jie Zhong, Chun He, Ronghua Zeng - Supercapacitive behavior of electrostatic self-assembly reduced graphene oxide/CoAl-layered double hydroxides nanocomposites, *Journal of Alloys and Compounds* **669** (2016) 146-155.
 17. Hang T. T. X., Duong N. T., Truc T.A., Hoang T., Thanh D. T. M., Daopiset S., Boonplean A. - Effects of hydrotalcite intercalated with corrosion inhibitor on cathodic disbonding of epoxy coatings, *Journal of Coatings Technology and Research* **12** (2015) 375-383.
 18. Hang T. T. X., Truc T. A., Duong N. T., Vu P. G., Hoang T. - Preparation and characterization of nanocontainers of corrosion inhibitor based on layered double hydroxides, *Applied Clay Science* **67-68** (2012) 18-25 .

19. Andreas Edenharter, Patrick Feicht, Bashar Diar-Bakerly, Günter Beyer, Josef Breu - Superior flame retardant by combining high aspect ratio layered double hydroxide and graphene oxide, *Polymer* **91** (2016) 41-49
20. Guobo Huang, Suqing Chen, Pingan Song, Pingping Lu, Chenglin Wu, Huading Liang - Combination effects of graphene and layered double hydroxides on intumescent flame-retardant poly(methyl methacrylate) nanocomposites, *Applied Clay Science* **88–89** (2014) 78–85.
21. Nguyen Thuy Duong, To Thi Xuan Hang, Arnaud Nicolay, Yoann Paint, Marie-Georges Olivier - Corrosion protection of carbon steel by solvent free epoxy coating containing hydrotalcites intercalated with different organic corrosion inhibitors, *Prog. Org. Coat.* **101** (2016) 331–341.
22. Esmaeili A., Entezari M. H. - Facile and fast synthesis of graphene oxide nanosheets via bath ultrasonic irradiation, *J. Colloid Interface Sci.* **432** (2014) 19–25.
23. Esmaeili a., Entezari M. H. - Facile and fast synthesis of graphene oxide nanosheets via bath ultrasonic irradiation, *J. Colloid Interface Sci.* **432** (2014) 19–25.
24. Xu, ZP, Braterman, PS, “Synthesis, structure and morphology of organic layered double hydroxide (LDH) hybrids: comparison between aliphatic anions and their oxygenated analogs.” *Appl. Clay Sci.* **48** 235-242 (2010)
25. Simons W. W. - Sadtler Research Laboratories, Inc., Pennsylvania, 1978.
26. Z. Liu, Z.M. Wang, X. Yang, K. Ooi - Intercalation of organic ammonium ions into layered graphite oxide, *Langmuir* **18** (12) (2002) 4926–4932.
27. U. Costantino, F. Marmottini, M. Nocchetti, R. Vivani - New synthetic routes to hydrotalcite-like compounds – Characterisation and properties of the obtained materials. *Eur. J. Inorg. Chem.* **10** (1998) 1439–1446.
28. Yinling Wang, Zhangcui Wang, Xiaoqin Wu, Xiaowang Liu, Maoguo Li - Synergistic effect between strongly coupled CoAl layered double hydroxides and graphene for the electrocatalytic reduction of oxygen, *Electrochimica Acta* **192** (2016) 196–204.