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ORIGINAL PAPER

Microencapsulation technology for thiourea corrosion inhibitor

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Abstract The microencapsulation technology was brought in to solidify corrosion inhibitor in order to prolong the releasing time of it. In this work, thiourea (H_2NCSNH_2) was used as a corrosion inhibitor and microcapsuled using glutin and polyvinyl alcohol (PVA), respectively, as protective agent. The re-sealing process was used as a way to prolong the releasing time of the H_2NCSNH_2 encapsulated in microcapsules. It was found that the H_2NCSNH_2 microcapsule corrosion inhibitor using PVA as a protective agent had a better releasing time. The releasing times of the H_2NCSNH_2 microcapsule corrosion inhibitors were prolonged from 18 to 48 h by re-sealing process and using PVA as a protective agent. Both the use of PVA as a protective agent and the application of the re-sealing process decreased the encapsulation efficiency of the H_2NCSNH_2. The performance parameters on protecting Q235 carbon steel from corrosion in 0.1-M H_2SO_4 solution were evaluated by polarization curve and electrochemical impedance spectra methods. The results showed that the H_2NCSNH_2 released into the solution from microcapsules could well protect Q235 carbon steel from corrosion and the corrosion-inhibiting mechanisms of it were the same as that of H_2NCSNH_2.

Keywords Microencapsulation technology · Corrosion · UV spectrophotometric method · Electrochemical impedance spectra · Polarization curve

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Introduction

Corrosion inhibitor technology is an effective and economic way for protecting metal from corrosion, which is already widely used in many industries [1–10]. The bottom of high sour gas wells, which have separators, cannot be well protected by liquid corrosion inhibitors. Solidifying and slowing their release rate would be an effective way to solve this problem. L. Mikhail Zheludkevich et al. [11] and A. N. Khramov et al. [12–13] had devoted their efforts to finding an effective way to control the releasing speed of corrosion inhibitors. L. Mikhail et al. [11] used zirconia nanoparticles as a reservoir for the storage and prolonged the releasing time of corrosion inhibitors. A. N. Khramov et al. [12–13] encapsulated the corrosion inhibitor within the coating matrix which slowed the release of them and then improved the protection capacity of the coating.

The microencapsulation technology is an effective way to solidify effective components and control the releasing speed of them which are encapsulated in microcapsules. With the development of it, the microencapsulation technology had been widely used in agriculture, food, medicine, and other industries because of its advantages

on solidifying effective components and slowing the releasing rate of them [14–19].

In this study work, the microencapsulation technology was applied to find an effective way to solidify and keep the thiourea (H_2NCSNH_2), which was encapsulated in microcapsule, releasing in a slow rate. Three kinds of microcapsules were made by using thermal phase separation method together with vigor Finestran drying bath method. The first and the second kinds were produced by using glutin and polyvinyl alcohol (PVA) as protective agents, respectively. And they were all sealed by alginate natrium once. The third kind used PVA as a protective agent and was sealed twice by alginate natrium. The qualities of them were evaluated by using UV spectrophotometric, polarization curve, and electrochemical impedance spectra (EIS) methods, respectively.

Experimental

Preparation of the microcapsules

Add a saturated H_2NCSNH_2 solution into a CH_2Cl_2 solution containing 85% ethyl cellulose. And then, add that mixture drop by drop into a 5% glutin solution or an 8% PVA solution until the W/O emulsion is formed. Maintain the emulsion at 60 °C and stir it until the CH_2Cl_2 is vaporized completely. After filtering, washing, and drying it, the primary product of the microcapsules is achieved [20, 21]. Dissolve the primary product in a 55 °C saturated alginate natrium solution and drop calcium chloride in it with an orifice device. Then, we get the H_2NCSNH_2 microcapsule corrosion inhibitors [22]. Three kinds of them were produced under three situations:

1. Product #1 was microencapsuled with glutin and was sealed once.
2. Product #2 was microencapsuled with PVA and was sealed once.
3. Product #3 was microencapsuled with PVA and was sealed twice.

Evaluation of the microcapsules

The pictures of the microcapsules were captured by a JT-2182II microscope.

Put 4 mg #1, 5 mg #2, and 6 mg #3 into 0.12-L 0.1-M H_2SO_4 solutions, respectively. The concentration of H_2NCSNH_2 ($C_{H_2NCSNH_2}$) released into the solutions was detected using UV spectrophotometric method [23] every 6 h.

The Q235 carbon steel electrode with a working surface area of 1 cm^2 was used as a working electrode in this study. The electrode was polished with silicon carbide waterproof electro-coated abrasive paper no. 1000, and then it was degreased with ethanol and dried in cool air before experiment. A titanium plating metal and a saturated calomel electrode were used as a counter electrode and a reference electrode, respectively. Polarization curve and EIS were measured using a computer-controlled system (CHI 604C). The working system was a three-electrode system. The polarization curve was performed at a scan rate of 0.3 mV s^{-1} and EIS was performed at the open circuit potential during the frequency of 0.05~100,000 Hz with an amplitude vibration of 5 mV. The polarization curve and the EIS were performed after the adding of microcapsules every 6 h. The polarization curve and EIS were also performed in 0.1-M H_2SO_4 solutions added with the H_2NCSNH_2 respectively at 0.31 mM and 0.438 mM, which equaled to the final concentrations of H_2NCSNH_2 in the

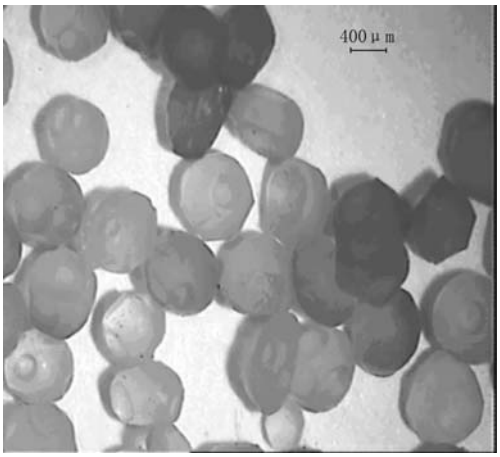

Fig. 1 Picture of H_2NCSNH_2 microcapsule corrosion inhibitor

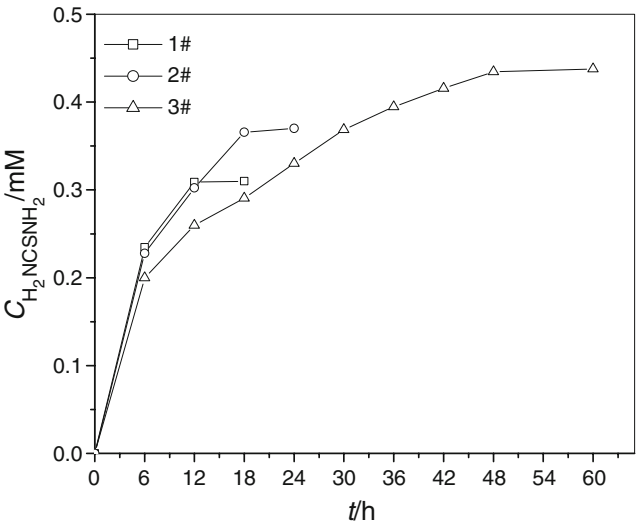

Fig. 2 Relationship between the concentration of H_2NCSNH_2 and time in 0.12-L 0.1-M H_2SO_4 solution containing 4 mg #1, 5 mg #2, and 6 mg #3 microcapsule corrosion inhibitor products, respectively

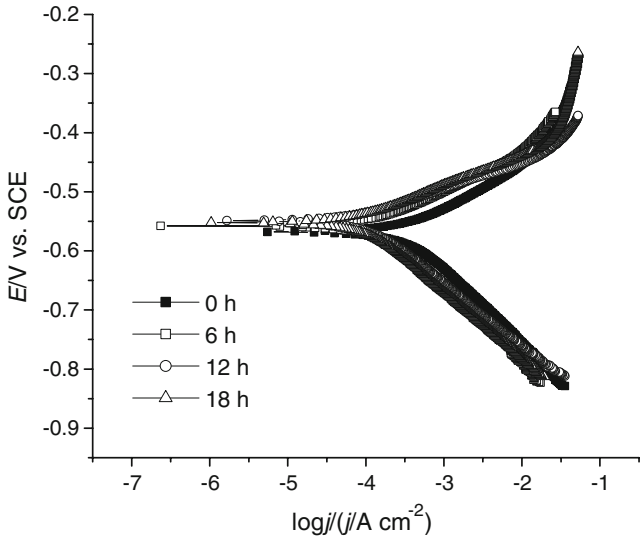

Fig. 3 Polarization curves obtained on Q235 carbon steel electrode determined in 0.12-L 0.1-M H_2SO_4 solution containing 4 mg #1 H_2NCSNH_2 microcapsule corrosion inhibitor every 6 h

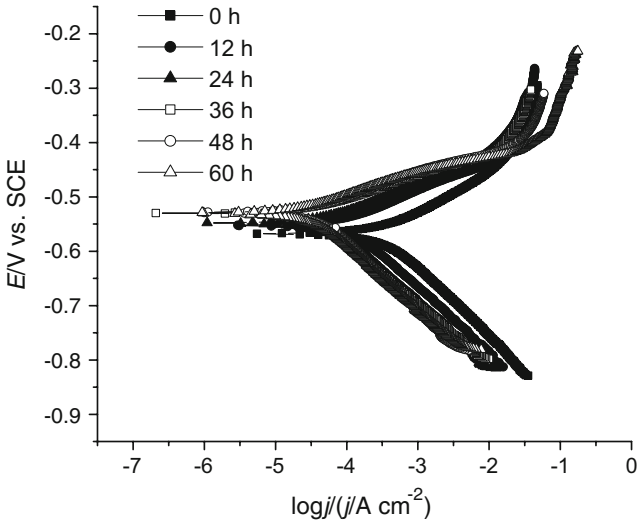

Fig. 5 Polarization curves obtained on Q235 carbon steel electrode determined in 0.12-L 0.1-M H_2SO_4 solution containing 6 mg #3 H_2NCSNH_2 microcapsule corrosion inhibitor every 6 h

systems added with #1 and #3 products. The polarization curve and the EIS were both calculated by ZView software.

All experiments were taken at the temperature of 28± 0.2 °C.

Results and discussion

The releasing rate

The shape and diameter of these three kinds of microcapsules were the same. Figure 1 was a picture of one kind of them. The picture showed that the diameter of it was about 500 μm and the shapes of them were granular which indicated that it was applicable to microencapsulate the H_2NCSNH_2 using the method mentioned above.

The relationship between $C_{H_2NCSNH_2}$ and time in 0.12-L 0.1-M H_2SO_4 solution was shown in Fig. 2. It could be found that the $C_{H_2NCSNH_2}$ increased with time until the H_2NCSNH_2 was released completely; then the $C_{H_2NCSNH_2}$ remained stable. This indicated that the microencapsulation technology could well prolong the releasing time of H_2NCSNH_2, which was encapsulated in microcapsules. The releasing time of #1, #2, and #3 were 12, 18, and 48 h, respectively. Therefore, the releasing time of the microcapsules microencapsulated with glutin was shorter than

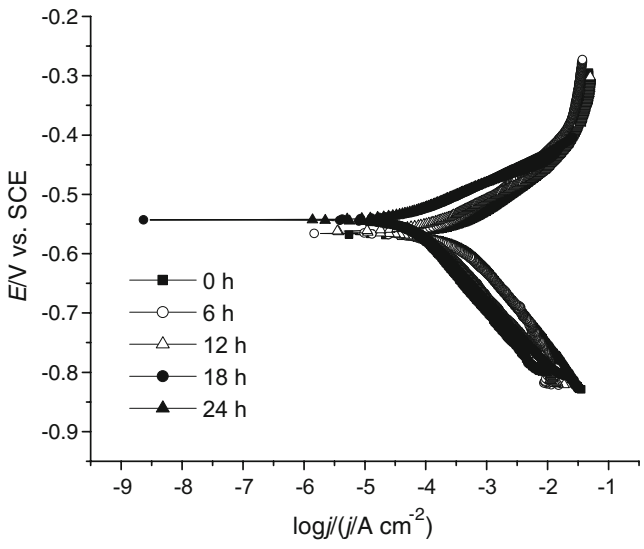

Fig. 4 Polarization curves obtained on Q235 carbon steel electrode determined in 0.12-L 0.1-M H_2SO_4 solution containing 5 mg #2 H_2NCSNH_2 microcapsule corrosion inhibitor every 6 h

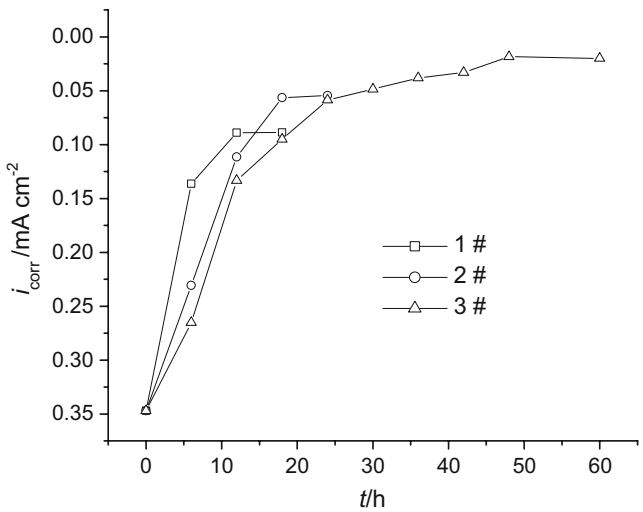

Fig. 6 Relation between i_{corr} calculated from Figs. 3, 4, and 5 and time

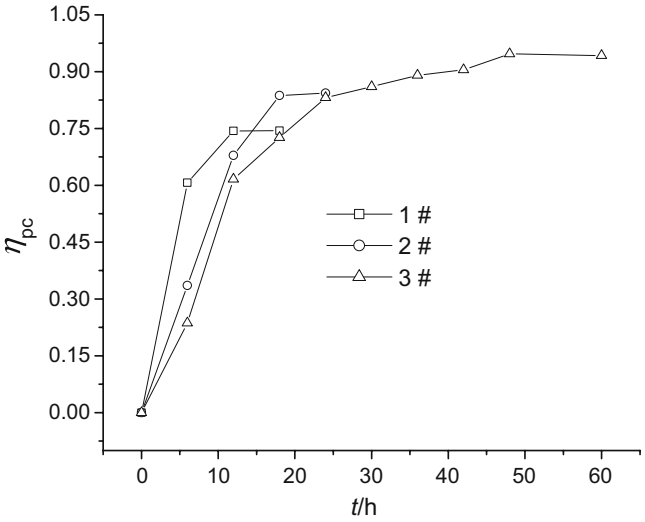

Fig. 7 Corrosion-inhibiting efficiency calculated from Fig. 6

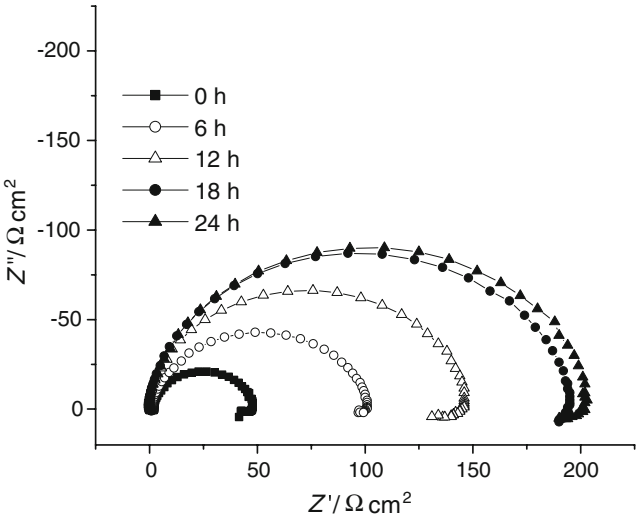

Fig. 9 EIS obtained on Q235 carbon steel electrode determined in 0.12-L 0.1-M H_2SO_4 solution containing 5 mg #2 H_2NCSNH_2 microcapsule corrosion inhibitor every 6 h

those with PVA. The re-sealing process could prolong the releasing time of the microcapsules from 18 to 48 h when microencapsuled with PVA. The $C_{H_2NCSNH_2}$ had no linear relationship with time. Therefore, the H_2NCSNH_2 was scattered in the microcapsules [24].

The encapsulation efficiency of the microcapsules could be calculated as Eq. 1 [25].

$$\eta_{H_2NCSNH_2} = \frac{m_{H_2NCSHNH_2}}{m_0} \times 100\% \quad (1)$$

Where $\eta_{H_2NCSNH_2}$ was the encapsulation efficiency of the H_2NCSNH_2; $m_{H_2NCSNH_2}$ was the weight of the H_2NCSNH_2; m_0 was the weight of the microcapsules. The encapsulation efficiencies of #1, #2, and #3 calculated from the results of Fig. 2 and Eq. 1 were 51.5%, 48.8%, and 44.7%, respectively.

It was obvious that the amount of H_2NCSNH_2 encapsulated in these three products in decreasing order was #3, #2, and #1. But the releasing speed of H_2NCSNH_2 in decreasing order was #1, #2, and #3.

Therefore, microcapsules microencapsulated with PVA had longer releasing time and slower releasing rate than those with glutin. The re-sealing process prolonged the releasing time and decreased the releasing rate. Both microencapsulating with PVA and re-sealing process decreased the encapsulation efficiency.

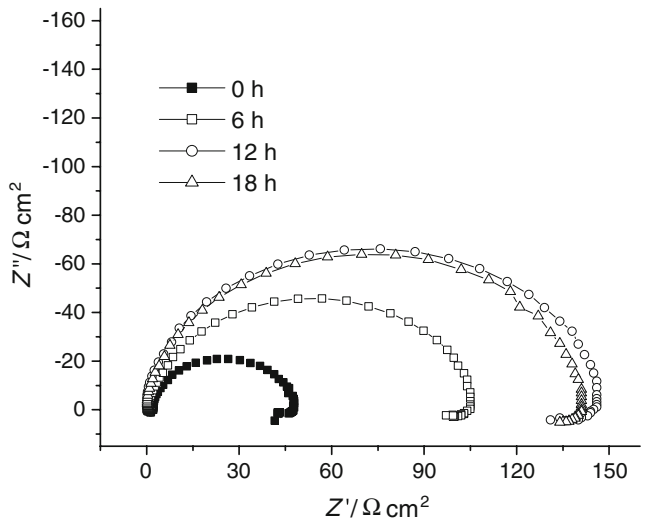

Fig. 8 EIS obtained on Q235 carbon steel electrode determined in 0.12-L 0.1-M H_2SO_4 solution containing 4 mg #1 H_2NCSNH_2 microcapsule corrosion inhibitor every 6 h

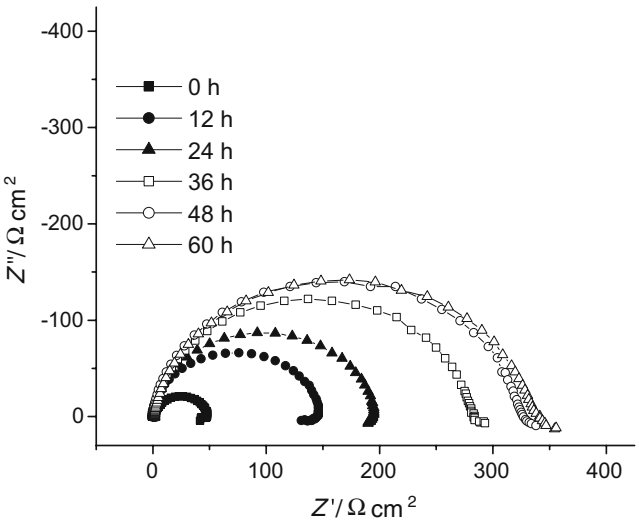

Fig. 10 EIS obtained on Q235 carbon steel electrode determined in 0.12-L 0.1-M H_2SO_4 solution containing 6 mg #3 H_2NCSNH_2 microcapsule corrosion inhibitor every 6 h

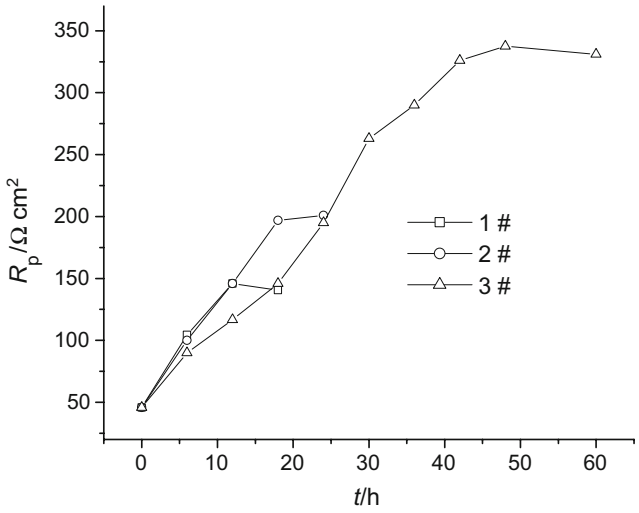

Fig. 11 Relation between i_{corr} calculated from Figs. 8, 9, and 10 and time

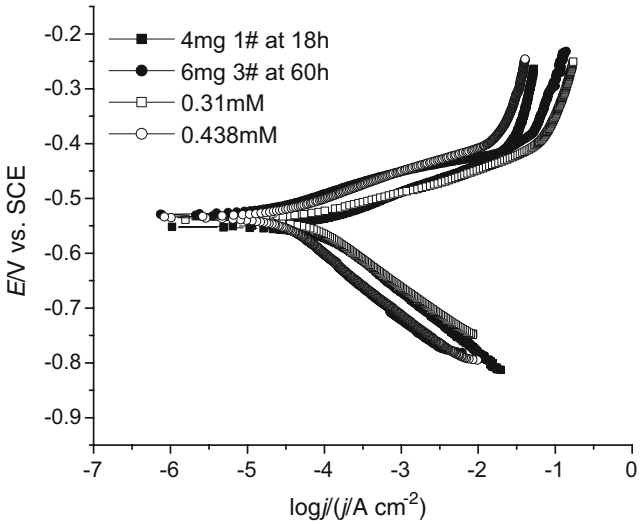

Fig. 13 Polarization curves obtained on Q235 carbon steel electrode in 0.12-L 0.1-M H_2SO_4 solutions containing H_2NCSNH_2, #1 and #3, respectively

Evaluation of the quality of the microcapsules using polarization curve

The polarization curve was used to evaluate the quality of these three kinds of microcapsules on protecting Q235 carbon steel from corrosion in 0.1-M H_2SO_4 solution and the results were shown in Figs. 3, 4, and 5. It could be found that the corrosion current densities decreased greatly at first with the releasing of the H_2NCSNH_2 and remained stable after 12 h for #1, 18 h for #2, and 48 h for #3. In other words, the releasing time of the H_2NCSNH_2 encapsulated in #1, #2, and #3 products are 12, 18, and 48 h, respectively. These results were all consistent with the results gotten from UV spectrophotometric method. The corrosion current densities calculated from Figs. 3, 4, and 5 were shown in Fig. 6, which showed that the H_2NCSNH_2 released could well protect Q235 carbon steel from corrosion and the corrosion rate decreased at first and then remained stable after 12, 18, and 48 h for #1, #2, and #3 products, respectively. The relative standard deviations of the potentials and the corrosion current densities are 4.15% and 11.4%, respectively.

The corrosion-inhibiting efficiency calculated from polarization curve (η_{pc}) could be calculated as follows [26]:

$$\eta_{pc} = \frac{i_{corr} - i_{corr}'}{i_{corr}} \times 100\% \quad (2)$$

Where i_{corr} and i_{corr}' were the corrosion current densities of the carbon steel in the system in the absence and in the presence of the microencapsulated corrosion inhibitors, respectively. The corrosion-inhibiting efficiencies calculated

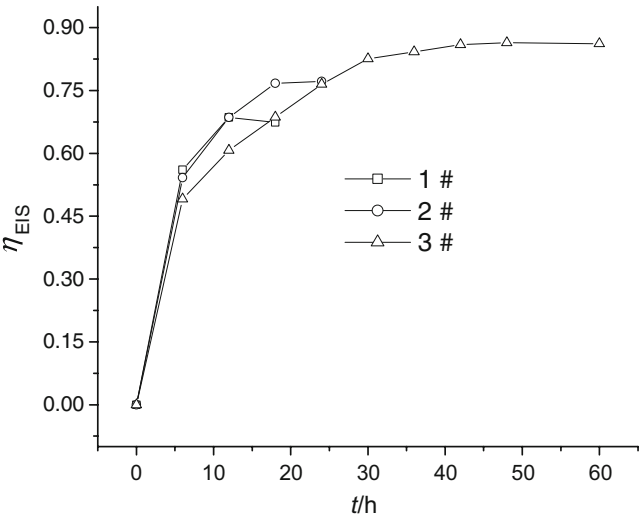

Fig. 12 Corrosion-inhibiting efficiency calculated from Fig. 11

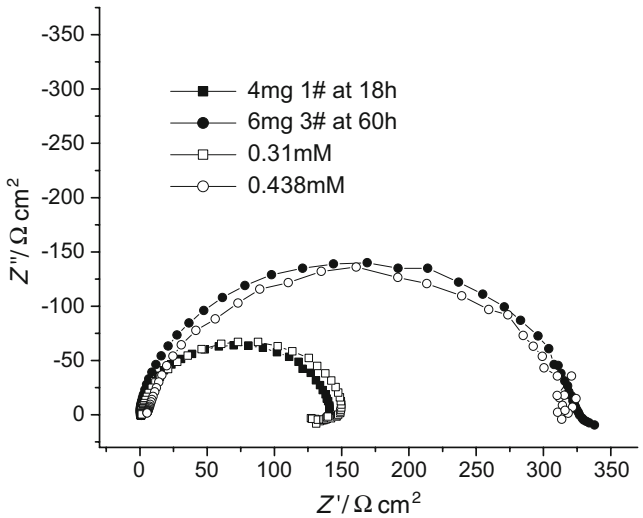

Fig. 14 EIS obtained on Q235 carbon steel electrode in 0.12-L 0.1-M H_2SO_4 solutions containing H_2NCSNH_2, #1 and #3, respectively

from the results of Fig. 6 and Eq. 2 were shown in Fig. 7. The corrosion-inhibiting efficiencies of #1, #2, and #3 all increased with time at first and then remained stable after 12, 18, and 48 h, respectively. These changes were all consistent with the changing of the values of the $C_{H_2NCSNH_2}$. It could also be concluded from Figs. 6 and 7 that the releasing rate of these three kinds of products in decreasing rate was #1, #2, and #3, which was well consistent with the results gotten from UV spectrophotometric method.

The values gotten from the polarization curves proved that the microencapsulation technology could solidify H_2NCSNH_2 and prolong and control the releasing rate of it. The H_2NCSNH_2 released could well inhibit the corrosion of Q235 carbon steel.

Evaluate the quality of the microcapsules using EIS method

EIS was performed after the three kinds of microcapsules were added into 0.12-L 0.1-M H_2SO_4 solutions every 6 h and the results were shown in Figs. 8, 9, and 10. It showed that the diameters of the arc, which equals to the values of R_p, increased with the releasing time at first and maintained a stable value after the H_2NCSNH_2 was released completely. Therefore, the corrosion rate, which was in proportion to the reciprocal of R_p, decreased with the release of the microcapsules and remained stable after the H_2NCSNH_2 was released completely. The values of R_p calculated from EIS were shown in Fig. 11, which expressed the inhibiting effects of the three kinds of microcapsules. The relative standard deviation of the values of R_p is 8.88%. It could also be concluded from Figs. 8, 9, and 10 that the releasing time of #1, #2, and #3 were 12, 18, and 48 h, respectively.

The corrosion-inhibiting efficiency calculated from EIS (η_{EIS}) could be evaluated as Eq. 3 [26]:

$$\eta_{EIS} = \left(1 - R_{p0}/R_p\right) \times 100\% \quad (3)$$

Where R_{p0} and R_p were polarization resistances calculated from EIS in the system in the absence and in the presence of the microencapsulated corrosion inhibitors, respectively. The corrosion-inhibiting efficiencies calculated from Eq. 3 were shown in Fig. 12. It was obvious that the changes of η_{EIS} were the same as that of η_{pc}.

Therefore, the results of EIS also proved that microencapsulating could well prolong the releasing time of H_2NCSNH_2 and could well control the corrosion rate of metal. These results were all well consistent with the results gotten from UV spectrophotometric method and polarization curves.

Comparison of the H_2NCSNH_2 and the H_2NCSNH_2 released from microcapsules

Figures 13 and 14 illustrated the polarization curve and the EIS in 0.1 M H_2SO_4 containing 0.31 and 0.438 mM H_2NCSNH_2 and in the solutions after adding #1 and #3 for 18 and 60 h, respectively. It could be concluded that the corrosion rates of Q235 carbon steel dipped into the solutions containing 0.31 and 0.438 mM H_2NCSNH_2 were the same as that in the solutions added with #1 and #3 for 18 and 60 h, respectively. The shapes of the polarization and the EIS in H_2NCSNH_2 solutions were the same as that in the solutions containing H_2NCSNH_2 microcapsule corrosion inhibitors. Therefore, the mechanisms of the H_2NCSNH_2 microcapsule corrosion inhibitors were the same as that of H_2NCSNH_2.

Conclusions

The microcapsule technology could solidify a corrosion inhibitor and control the releasing rate of it. H_2NCSNH_2 microcapsule corrosion inhibitors could well inhibit the corrosion of metal. Microencapsulating H_2NCSNH_2 with PVA had a longer releasing time and a slower releasing rate than that using glutin. The re-sealing process could prolong the releasing time and slow the releasing rate of H_2NCSNH_2. Both microencapsulating with PVA and re-sealing could decrease the encapsulation efficiency of H_2NCSNH_2 microcapsule corrosion inhibitors. The corrosion-inhibiting mechanisms of H_2NCSNH_2 microcapsule corrosion inhibitors were the same as that of H_2NCSNH_2.

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References

1. Finšgar M, Lesar A, Kokalj A, Milošev I (2008) Electrochim Acta 53:8287. doi:10.1016/j.electacta.2008.06.061
2. Khaled KF (2008) Mater Chem Phys 112:104. doi:10.1016/j.matchemphys.2008.05.052
3. Keles H, Keles M, Dehri I, Serindag O (2008) Mater Chem Phys 112:173. doi:10.1016/j.matchemphys.2008.05.027
4. Kellou-Kerkouche F, Benchettara A, Amara S (2008) Mater Chem Phys 110:26. doi:10.1016/j.matchemphys.2008.01.005
5. Al-Sarawy AA, Fouda AS, Shehab El-Dein WA (2008) Desalination 229:279. doi:10.1016/j.desal.2007.09.013

6. Solmaz R, Kardaş G, Çulha M, Yazıcı B, Erbil M (2008) Electrochimica Acta 53:5941. doi:10.1016/j.electacta.2008.03.055
7. Machnikova E, Whitmire KH, Hackerman N (2008) Electrochim Acta 53:6024. doi:10.1016/j.electacta.2008.03.021
8. Olivares-Xometl O, Likhanova NV, Domínguez-Aguilar MA, Arce E, Dorantes H, Arellanes-Lozada P (2008) Mater Chem Phys 110:344. doi:10.1016/j.matchemphys.2008.02.010
9. Amar H, Braisaz T, Villemin D, Moreau B (2008) Mater Chem Phys 110:1. doi:10.1016/j.matchemphys.2007.10.001
10. Noor EA, Al-Moubarak AH (2008) Mater Chem Phys 110:145. doi:10.1016/j.matchemphys.2008.01.028
11. Zheludkevich ML, Serra R, Montemor MF, Ferreira MGS (2005) Electrochem Commun 7:836. doi:10.1016/j.elecom.2005.04.039
12. Khramov AN, Voevodin NN, Balbyshev VN, Donley MS (2004) Thin Solid Films 447–448:549. doi:10.1016/j.tsf.2003.07.016
13. Khramov AN, Voevodin NN, Balbyshev VN, Mantz RA (2005) Thin Solid Films 483:191. doi:10.1016/j.tsf.2004.12.021
14. Allan-Wojtas P, Hansen LT, Paulson AT (2008) LWT Food Sci Technol 41:101
15. Espinosa EP, Barillé L, Allam B (2007) J Exp Mar Biol Ecol 343:118. doi:10.1016/j.jembe.2006.12.002
16. Yúfera M, Fernández-Díaz C, Pascua E (2005) Aquaculture 248:253. doi:10.1016/j.aquaculture.2005.04.026
17. Blasi P, Giovagnoli S, Schoubben A, Ricci M, Rossi C, Luca G, Basta G, Calafiore R (2006) Int J Pharm 324:27. doi:10.1016/j.ijpharm.2006.07.049
18. Brannon-Peppas L (1994) J Control Release 31:307. doi:10.1016/0168-3659(94)90013-2
19. Yamada T, Onishi H, Machida Y (2001) J Control Release 75:271. doi:10.1016/S0168-3659(01)00399-6
20. Naik R, Joshi P, Umbarkar S, Deshpande RK (2005) Catal Commun 6:125. doi:10.1016/j.catcom.2004.11.010
21. Fernandes CM, Ramos P, Falcão AC, Veiga FJB (2003) J Control Release 88:127. doi:10.1016/S0168-3659(02)00465-0
22. Shi X-Y, Tan T-W (2002) Biomaterials 23:4469. doi:10.1016/S0142-9612(02)00165-5
23. Rosales D, Millan I, Ariza JLG (1986) Talanta 33:607. doi:10.1016/0039-9140(86)80138-2
24. Lewis DH, Cowsar DR (1977) Principles of controlled release pesticides. In: Scher HB (ed) ACS symposium series, vol. 53. American Chemical Society, Washington D.C., pp 1–16
25. Nii T, Ishii F (2005) Int J Pharm 298:198. doi:10.1016/j.ijpharm.2005.04.029
26. Benmessaoud M, Es-salah K, Hajjaji N, Takenouti H, Srhiri A, Ebentouhami M (2007) Corros Sci 49:3880. doi:10.1016/j.corsci.2007.03.017