Corrosion resistance of graphene/waterborne epoxy composite coatings in CO₂-saturated NaCl solution

Hao Xu, Haijun Hu, Hongmei Wang, Yongjun Li and Yun Li

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Review timeline
Original submission: 26 November 2019
1st revised submission: 11 March 2020
2nd revised submission: 28 March 2020
Final acceptance: 3 April 2020

Note: Reports are unedited and appear as submitted by the referee. The review history appears in chronological order.

Review History

RSOS-191943.R0 (Original submission)

Review form: Reviewer 1

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Accept with minor revision (please list in comments)
Comments to the Author(s)
This paper is very interesting and the topic is of highly significance. I recommend a minor revision before its acceptance. The comments and suggestions are as follows.

1. Section 3.2: “The fitting results of polarization curves…” should be modified as “The parameters obtained from the Tafel extrapolation method…”. And in Table 2, I suggest to remove the Rp since if you want to get a precise Rp, a special LPR measurement is required.
2. Please mark all of the peaks in Raman and FTIR.
3. The caption of Figure 4 should be: The cross-sectional SEM image…

Review form: Reviewer 2

Is the manuscript scientifically sound in its present form? Yes

Are the interpretations and conclusions justified by the results? Yes

Is the language acceptable? Yes

Do you have any ethical concerns with this paper? No

Have you any concerns about statistical analyses in this paper? No

Recommendation?
Major revision is needed (please make suggestions in comments)

Comments to the Author(s)
The authors describe the development and study of an anti-corrosion, CO2 resistance coating for use in oil and gas industry. The coating consists of a waterborne epoxy with various graphene loadings. The results show that the addition of graphene enhanced the uniformity of the coating and electrochemical testing demonstrated an enhancement in corrosion resistance. The assignment of polarisation curve gradient to diffusion of Fe ions is highly speculative and such effects can be due to a number of processes. The authors should justify this further before publication.

1) The discussion of SEM results refers to micropores. Typically, this implies less than 2 nm in pore diameter but here is used to describe larger pores

Decision letter (RSOS-191943.R0)

28-Feb-2020

Dear Dr Xu:

Title: Corrosion Resistance of Graphene/Waterborne Epoxy Composite Coatings in CO2-saturated NaCl Solution
Thank you for submitting the above manuscript to Royal Society Open Science. On behalf of the Editors and the Royal Society of Chemistry, I am pleased to inform you that your manuscript will be accepted for publication in Royal Society Open Science subject to minor revision in accordance with the referee suggestions. Please find the reviewers’ comments at the end of this email. I apologise that this has taken longer than usual.

The reviewers and handling editors have recommended publication, but also suggest some minor revisions to your manuscript. Therefore, I invite you to respond to the comments and revise your manuscript.

Because the schedule for publication is very tight, it is a condition of publication that you submit the revised version of your manuscript before 08-Mar-2020. Please note that the revision deadline will expire at 00.00am on this date. If you do not think you will be able to meet this date please let me know immediately.

To revise your manuscript, log into https://mc.manuscriptcentral.com/rsos and enter your Author Centre, where you will find your manuscript title listed under "Manuscripts with Decisions". Under "Actions," click on "Create a Revision." You will be unable to make your revisions on the originally submitted version of the manuscript. Instead, revise your manuscript and upload a new version through your Author Centre.

When submitting your revised manuscript, you will be able to respond to the comments made by the referees and upload a file "Response to Referees" in "Section 6 - File Upload". You can use this to document any changes you make to the original manuscript. In order to expedite the processing of the revised manuscript, please be as specific as possible in your response to the referees.

When uploading your revised files please make sure that you have:

1) A text file of the manuscript (tex, txt, rtf, docx or doc), references, tables (including captions) and figure captions. Do not upload a PDF as your "Main Document".
2) A separate electronic file of each figure (EPS or print-quality PDF preferred (either format should be produced directly from original creation package), or original software format)
3) Included a 100 word media summary of your paper when requested at submission. Please ensure you have entered correct contact details (email, institution and telephone) in your user account
4) Included the raw data to support the claims made in your paper. You can either include your data as electronic supplementary material or upload to a repository and include the relevant doi within your manuscript
5) All supplementary materials accompanying an accepted article will be treated as in their final form. Note that the Royal Society will neither edit nor typeset supplementary material and it will be hosted as provided. Please ensure that the supplementary material includes the paper details where possible (authors, article title, journal name).

Supplementary files will be published alongside the paper on the journal website and posted on the online figshare repository (https://figshare.com). The heading and legend provided for each supplementary file during the submission process will be used to create the figshare page, so please ensure these are accurate and informative so that your files can be found in searches. Files on figshare will be made available approximately one week before the accompanying article so that the supplementary material can be attributed a unique DOI.

Once again, thank you for submitting your manuscript to Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal
Society of Chemistry. I look forward to receiving your revision. If you have any questions at all, please do not hesitate to get in touch.

Best wishes,
Dr Laura Smith
Publishing Editor, Journals

Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Dr Darren Walsh.

******************************************

RSC Associate Editor:
Comments to the Author:
(There are no comments.)

RSC Subject Editor:
Comments to the Author:
(There are no comments.)

******************************************

Reviewer comments to Author:
Reviewer: 1

Comments to the Author(s)
This paper is very interesting and the topic is of highly significance. I recommend a minor revision before its acceptance. The comments and suggestions are as follows.

1. Section 3.2: “The fitting results of polarization curves…” should be modified as “The parameters obtained from the Tafel extrapolation method…”. And in Table 2, I suggest to remove the Rp since if you want to get a precise Rp, a special LPR measurement is required.
2. Please mark all of the peaks in Raman and FTIR.
3. The caption of Figure 4 should be: The cross-sectional SEM image...

Reviewer: 2

Comments to the Author(s)
The authors describe the development and study of an anti-corrosion, CO2 resistance coating for use in oil and gas industry. The coating consists of a waterborne epoxy with various graphene loadings. The results show that the addition of graphene enhanced the uniformity of the coating and electrochemical testing demonstrated an enhancement in corrosion resistance. The assignment of polarisation curve gradient to diffusion of Fe ions is highly speculative and such effects can be due to a number of processes. The authors should justify this further before publication.

1) The discussion of SEM results refers to micropores. Typically, this implies less than 2 nm in pore diameter but here is used to describe larger pores
Author's Response to Decision Letter for (RSOS-191943.R0)

See Appendix A.

Decision letter (RSOS-191943.R1)

26-Mar-2020

Dear Dr Xu:

Title: Corrosion Resistance of Graphene/Waterborne Epoxy Composite Coatings in CO2-saturated NaCl Solution
Manuscript ID: RSOS-191943.R1

Thank you for submitting the above manuscript to Royal Society Open Science. On behalf of the Editors and the Royal Society of Chemistry, I am pleased to inform you that your manuscript will be accepted for publication in Royal Society Open Science subject to minor revision in accordance with the referee suggestions. Please find the reviewers’ comments at the end of this email.

The reviewers and handling editors have recommended publication, but also suggest some minor revisions to your manuscript. Therefore, I invite you to respond to the comments and revise your manuscript.

Because the schedule for publication is very tight, it is a condition of publication that you submit the revised version of your manuscript before 04-Apr-2020. Please note that the revision deadline will expire at 00.00am on this date. If you do not think you will be able to meet this date please let me know immediately.

To revise your manuscript, log into https://mc.manuscriptcentral.com/rsos and enter your Author Centre, where you will find your manuscript title listed under “Manuscripts with Decisions”. Under "Actions," click on "Create a Revision." You will be unable to make your revisions on the originally submitted version of the manuscript. Instead, revise your manuscript and upload a new version through your Author Centre.

When submitting your revised manuscript, you will be able to respond to the comments made by the referees and upload a file "Response to Referees" in “Section 6 - File Upload”. You can use this to document any changes you make to the original manuscript. In order to expedite the processing of the revised manuscript, please be as specific as possible in your response to the referees.

When uploading your revised files please make sure that you have:
1) A text file of the manuscript (tex, txt, rtf, docx or doc), references, tables (including captions) and figure captions. Do not upload a PDF as your "Main Document".
2) A separate electronic file of each figure (EPS or print-quality PDF preferred (either format should be produced directly from original creation package), or original software format)
3) Included a 100 word media summary of your paper when requested at submission. Please ensure you have entered correct contact details (email, institution and telephone) in your user account
4) Included the raw data to support the claims made in your paper. You can either include your data as electronic supplementary material or upload to a repository and include the relevant doi within your manuscript
5) All supplementary materials accompanying an accepted article will be treated as in their final form. Note that the Royal Society will neither edit nor typeset supplementary material and it will
be hosted as provided. Please ensure that the supplementary material includes the paper details where possible (authors, article title, journal name).

Supplementary files will be published alongside the paper on the journal website and posted on the online figshare repository (https://figshare.com). The heading and legend provided for each supplementary file during the submission process will be used to create the figshare page, so please ensure these are accurate and informative so that your files can be found in searches. Files on figshare will be made available approximately one week before the accompanying article so that the supplementary material can be attributed a unique DOI.

Once again, thank you for submitting your manuscript to Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry. I look forward to receiving your revision. If you have any questions at all, please do not hesitate to get in touch.

Kind regards,
Dr Laura Smith
Publishing Editor, Journals
Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Dr Darren Walsh.

***************************************************************************

RSC Associate Editor
Comments to the Author:
Please see attached

***************************************************************************

Reviewer comments to Author:

Author's Response to Decision Letter for (RSOS-191943.R1)
See Appendix B.

Decision letter (RSOS-191943.R2)

03-Apr-2020

Dear Dr Xu:

Title: Corrosion Resistance of Graphene/Waterborne Epoxy Composite Coatings in CO2-saturated NaCl Solution
Manuscript ID: RSOS-191943.R2

It is a pleasure to accept your manuscript in its current form for publication in Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry.

The comments of the reviewer(s) who reviewed your manuscript are included at the end of this email.

Thank you for your fine contribution. On behalf of the Editors of Royal Society Open Science and the Royal Society of Chemistry, I look forward to your continued contributions to the Journal.

Yours sincerely,
Dr Laura Smith
Publishing Editor, Journals

Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Dr Darren Walsh.

******

RSC Associate Editor
Comments to the Author:
(There are no comments.)

******

Reviewer(s)' Comments to Author:
Appendix A

Dear Editors and Reviewers,

Thank you very much for taking your time to review this manuscript. I really appreciate all your comments and suggestions. The manuscript (Manuscript ID: RSOS-191943) has been revised by taking all these suggestions into account.

Here are responses to the reviewer comments:

Reviewer #1:

Question 1. Section 3.2: “The fitting results of polarization curves…” should be modified as “The parameters obtained from the Tafel extrapolation method…”. And in Table 2, I suggest to remove the R_p since if you want to get a precise R_p, a special LPR measurement is required.

Answer 1: Thank you for your nice comments on our article. According to your suggestions, the expression of polarization curves in section 3.2 has been modified and the R_p in Table 2 has been removed.

Fixed 1: (Section 3.2, line 3) The parameters obtained from the Tafel extrapolation method are shown in Table 2, in which I_corr and E_corr stand for the corrosion current density and the corrosion potential respectively. R_p represents the polarization resistance. B_a and B_c represent the slope of the anodic and cathodic polarization respectively.

Question 2. Please mark all of the peaks in Raman and FTIR.

Answer 2: We have added all the functional groups corresponding to the characteristic peaks in section 3.1.

Fixed 2: (Section 3.1, paragraph 3, line 3) The peak near 2800-3000 cm^{-1} was due to the C-H vibration of aliphatic group. The peak in 1244 cm^{-1} and the broad absorption at 3382 cm^{-1} were assigned to C-O-C and –OH respectively. Absorption at 916 cm^{-1} and 827 cm^{-1} were assigned to epoxy groups.

Question 3. The caption of Figure 4 should be: The cross-sectional SEM image…

Answer 3: The caption of Figure 4 has been modified as “The cross-sectional SEM image of 0.5 wt% graphene/waterborne epoxy composite coating on the steel 1020 test surface.”

Fixed 3: (Figure 4, caption) Figure 4. The cross-sectional SEM image of 0.5 wt% graphene/waterborne epoxy composite coating on the steel 1020 test surface.

Reviewer #2:

Question 1. The assignment of polarization curve gradient to diffusion of Fe ions is highly speculative and such effects can be due to a number of processes. The authors should justify this further before publication.

Answer 1: We highly appreciate for your professional review work on our article. As you are concerned, we have not fully discussed the correlation between the slope of polarization curve and the diffusion of iron ions in this work. That is because we discussed this issue in our previous work (H. J. Hu, H. Xu, Y. J. Li, X. Chen, Y. Li, Corrosion NACE. Paper No.13212(2019). Appendix 1).

In this work, the line scan by EDS of mild steel coated with 0.5%wt graphene/waterborne epoxy
composite coating and neat waterborne epoxy were measured after immersed in high chlorine CO\textsubscript{2} saturated solution. And we compared the intensity of Fe element inside of the different coatings within 2 \( \mu \text{m} \) (figure 1). It can be observed that with the addition of graphene, the intensity of Fe element of 0.5\%wt graphene/epoxy composite coating is stronger than that of the pure epoxy coating. We suppose the increase in intensity indicates the deposition of iron ions at the interface of the substrate metal and the composite coating. And The increase of slope of the anodic polarization \( B_a \) indicates the transition of anodic reaction. Therefore, we came to a conclusion that the graphene dispersed inside the composite coating retarded the diffusion of iron ions and thus the anodic reaction. The work was cited in the revised manuscript.

![Graph showing the intensity of Fe element inside of the different coatings within 2 \( \mu \text{m} \).](image)

**Figure 1:** The intensity of Fe element inside of the different coatings within 2 \( \mu \text{m} \).

### Fixed 1:

*(Abstract)* This study investigated the corrosion resistance of graphene/waterborne epoxy composite coatings in CO\textsubscript{2}-saturated NaCl solution. The coatings were prepared by dispersing graphene in waterborne epoxy with the addition of carboxymethylcellulose sodium. The structure and composition of the coatings were characterized by SEM, TEM, FTIR and Raman spectroscopies. The corrosion resistance of the composite coatings was investigated by potentiodynamic polarization measurements and electrochemical impedance spectroscopy. Composite coatings with more uniform surfaces and far fewer defects than blank waterborne epoxy coatings were obtained on 1020 steel. The 0.5 \( \text{wt\%} \) graphene/waterborne epoxy composite coating exhibited much lower corrosion rate and provided better water resistance properties and long-term protection than those of the blank epoxy coating in CO\textsubscript{2}-saturated NaCl solution. This was attributed to the distribution of graphene inside the composite coating that retarded the diffusion of iron ions and thus the anodic reaction.

*(Section 3.2, line 16)* Table 1 shows that \( B_a \) increased with the addition of graphene while \( B_c \) did not change significantly. The increase of \( B_a \) indicates the transition of anodic reaction. With the addition of graphene, the intensity of Fe element of graphene/epoxy composite coating at the interface of the substrate metal and the composite coating is stronger than that of the pure epoxy coating. And the increase in the intensity of Fe element indicates the deposition of iron ions at the interface [28]. Therefore, the graphene distributed inside the composite coating was thought to impede the diffusion of Fe ions which retarded the anodic reaction.

*(References)* [28] H. J. Hu, H. Xu, Y. J. Li, X. Chen, Y. Li, Corrosion NACE. Paper No.13212(2019).
Question 2. The discussion of SEM results refers to micropores. Typically, this implies less than 2 nm in pore diameter but here is used to describe larger pores.

Answer 2: Thank you for pointing out the inaccuracy of our choice of words. The expression of “micropores” has been modified as “pores”.

Fixed 2: (Section 3.1, paragraph 6, line 3) The SEM image of the blank waterborne epoxy coating in Figure 5(a) showed a surface topography containing many pores and inhomogeneous defects that is due to the rapid water evaporation during the curing process of waterborne epoxy coatings. These pores and defects will serve as active channels for aggressive species and it is not surprised that the corrosion resistance of waterborne epoxy coatings are significantly lower than those of solvent-based epoxy coatings.

We have corrected them in the revised manuscript by underlining and marking with blue. Thank you again for your consideration of our work!

Yours Sincerely,

Haijun Hu
Xi’an Jiaotong University, Xi’an 710049, China
Appendix 1:

H. J. Hu, H. Xu, Y. J. Li, X. Chen, Y. Li, Corrosion NACE. Paper No.13212(2019).

Study of CO₂-corrosion Behavior of Graphene/Epoxy Composite Coating in High Chloride Environment

Haijun Hu¹, Hao Xu², Xuefeng Li³, Xiaogang Yin², Yun Li³
¹ Xi’an Jiaotong University
NO. 28 Xianyang West Rd
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ABSTRACT

Graphene/epoxy composite coatings are prepared through dispersing graphene in waterborne epoxy coatings to investigate the CO₂ corrosion behavior in a high chloride environment. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) are used to characterize the composite coatings. The corrosion protection performance is studied by electrochemical impedance spectroscopy (EIS) and by measurement of the polarization curve. Results show that the addition of graphene improved the anti-corrosion properties of the composite coatings. The corrosion potential (Ecorr) of the 0.5% graphene/epoxy composite coating (Ecorr = -444.78 mV) was more positive than that of the epoxy coating (Ecorr = -495.76 mV). The anodic reaction was retarded owing to graphene distributed inside the composite coating that impeded the diffusion of iron ions, while the cathodic reactions were much less affected.

Keywords: epoxy coating, graphene, CO₂ corrosion, high chloride

INTRODUCTION

Carbon dioxide flooding as a tertiary recovery method has been widely used all over the world because of its wide application range, high displacement efficiency and...
Figure 4: The distribution of elements along the depth of mild steel coated with epoxy after electrochemical measurements.

Figure 2 shows the results of the line scan by EDX of mild steel coated with 0.5%wt graphene/epoxy composite coating and the distribution of elements along the depth can be observed in Figure 3. Correspondingly, Figure 4 shows the distribution of elements of mild steel coated with pure epoxy after electrochemical measurements. Take the position marked in the figure as the origin, and compare the intensity of Fe of different coatings both inside of the base metal and coatings within 2 μm. The results are shown in Figure 5 and Figure 6, respectively. It can be clearly observed that with the addition of graphene, the intensity of Fe of 0.5%wt graphene/epoxy composite coating is two to three times stronger than that of the pure epoxy coating. The increase in intensity indicates the deposition of iron ions at the interface of the substrate metal and the composite coating which demonstrates the barrier effect of the graphene distributed inside the composite coating on the diffusion of iron ions.
Appendix B

Dear Editors and Reviewers,
Thank you very much for taking your time to review this manuscript. We really appreciate all your comments and suggestions. The manuscript (Manuscript ID: RSOS-191943.R1) has been revised by taking all these suggestions into account.
Here are responses to the comments:
Question 1. The quantities in the tables of data must be converted into standard scientific notation. The authors have used terms such as 6.21E-4 throughout. This is not correct and this example should be presented as 6.21 \times 10^{-4}. Please do this for all quantities throughout the manuscript.

Answer 1: Thank you for pointing out the mistake. According to your suggestions, all the quantities in the tables of data have been converted into standard scientific notation.

Fixed 1:

Table 2. Parameters obtained from polarization curves in Figure 6.

|                | Bare steel 1020 | Blank Waterborne Epoxy | 0.25%wt Graphene/Epoxy Composite | 0.5%wt Graphene/Epoxy Composite |
|----------------|-----------------|------------------------|----------------------------------|---------------------------------|
| Corrosion Rate (mm/a) | 0.381           | 7.93 \times 10^{-4}    | 1.64 \times 10^{-4}              | 4.99 \times 10^{-5}             |
| \(I_{corr}\) (amps/cm²) | 3.73 \times 10^{-5} | 6.74 \times 10^{-8}    | 1.39 \times 10^{-8}              | 4.24 \times 10^{-9}             |
| \(E_{corr}\) (Volts)    | -0.705          | -0.676                 | -0.639                           | -0.604                          |
| \(B_a\) (mV/dec)        | 41.3            | 84.7                   | 128                              | 167                             |
| \(B_c\) (mV/dec)        | -357            | -329                   | -289                             | -345                            |
| \(\eta\)               | -               | 99.79%                 | 99.96%                           | 99.98%                          |

Table 3. Fitting results from the EIS measurements in Figure 8.

| Time /h | \(R_c/(\Omega \cdot \text{cm}^2)\) | \(Q_c/(\mu \text{F} \cdot \text{cm}^2)\) | \(R_c/(k\Omega \cdot \text{cm}^2)\) | \(Q_{dl}/(\mu \text{F} \cdot \text{cm}^2)\) | \(R_{ct}/(k\Omega \cdot \text{cm}^2)\) |
|---------|-----------------------------------|------------------------------------------|------------------------------------|------------------------------------------|-----------------------------------|
| 2       | 4.23                              | 0.647                                    | 9.70                               | 1.03                                     | 48.5                              |
| 12      | 4.29                              | 1.67                                     | 3.82                               | 6.27                                     | 43.3                              |
| 24      | 3.79                              | 3.49                                     | 1.33                               | 14.5                                     | 39.8                              |
| 48      | 4.86                              | 4.97                                     | 0.961                              | 19.3                                     | 30.3                              |
| 72      | 4.46                              | 5.56                                     | 0.687                              | 28.3                                     | 25.2                              |
| 96      | 3.99                              | 6.11                                     | 0.445                              | 40.2                                     | 24.6                              |

Epoxy

| 0.25%wt | 2 | 3.32 | 3.30 \times 10^{-4} | 45.2 | 2.71 \times 10^{-2} | 82.04 |

Appendix B
|                  |     |          |       |          |       |
|------------------|-----|----------|-------|----------|-------|
| **Graphene/Epox Composite** | 12  | 4.28     | 4.94×10^-4 | 42.7    | 5.63×10^-2 | 69.91 |
|                  | 24  | 4.37     | 5.47×10^-4 | 39.3    | 3.94×10^-2 | 60.52 |
|                  | 48  | 4.96     | 5.59×10^-4 | 30.0    | 6.17×10^-2 | 42.43 |
|                  | 72  | 3.92     | 6.21×10^-4 | 23.5    | 1.64      | 93.87 |
|                  | 96  | 4.75     | 6.34×10^-4 | 20.9    | 1.85      | 60.01 |
| **0.5%wt Graphene/Epox Composite** | 2   | 3.98     | 7.53×10^-4 | 227     | 1.26×10^-2 | 1371 |
|                  | 12  | 3.78     | 8.72×10^-4 | 161     | 1.38×10^-2 | 1290 |
|                  | 24  | 4.45     | 9.83×10^-4 | 156     | 1.60×10^-2 | 1192 |
|                  | 48  | 4.60     | 9.97×10^-4 | 142     | 1.71×10^-2 | 1091 |
|                  | 72  | 4.65     | 9.76×10^-4 | 122     | 1.83×10^-2 | 1166 |
|                  | 96  | 4.87     | 1.17×10^-3 | 117     | 2.55×10^-2 | 896  |

Thank you again for considering our article for publication in *Royal Society Open Science.*
Yours Sincerely,

Haijun Hu
Xi’an Jiaotong University, Xi’an 710049, China