jz-2021-03958h.R1

Name: Peer Review Information for "Probing the Polysulfide Confinement in Two Different Sulfur Host for Mg|S Battery Employing Operando Raman and Ex situ UV-Visible Spectroscopy"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author

1. Major advance of the paper:

The authors present findings from experiments using carbon nanotubes (CNT) as a cathode material for Mg-S batteries. CNT-based cathodes show improved cyclability, reduced overpotentials, and less polysulfide formation (verified with UV-vis absorption spectroscopy). This performance is compared with literature and shown to be an improvement of the state of the art (see Figure S12)

2. The immediate significance of this advance:

The synthesis method of CNT-S cathodes is reported along with improved cycling performance.

3. Technical suggestions:

a. The authors report operando Raman spectra of the CNT-sulfur cathode during cycling as evidence of polysulfide confinement in CNTs. For example, on page 6 the authors claim “The bands at 153cm-1 and 219cm-1 are attributed to the presence of higher order polysulfides which confirms the confinement of higher order polysulfides inside the carbon nanotubes of CNT-S cathode”. While the reduced PS concentration seen in the UV-vis measurements indicate improved confinement, I do not believe the Raman spectra demonstrates this, at least not in the way the authors claim. The Raman spectra shown agrees well with other Raman measurements of dissolved polysulfides in the literature (For example, liquid-phase Raman spectra of polysulfides are reported in “Raman Spectroscopy Study of the Reaction between Sodium Sulfide or Disulfide and Sulfur: Identity of the Species Formed in Solid and Liquid Phases” https://pubs.acs.org/doi/pdf/10.1021/ic9900096, and operando measurements show similar results in “In Situ Raman Spectroscopy of Sulfur Speciation in Lithium−Sulfur Batteries” https://pubs.acs.org/doi/pdf/10.1021/am5072942.). EDS measurements report at least 6% sulfur outside of the CNT even after repeated washing, and it is likely that this external sulfur is largely responsible for the Raman results.

b. I also found the paper lacking in rigor. For example, on page 2 the authors state that polysulfide dissolution is an “even greater challenge impeding the success of Mg|S batteries” and become “even more important for the development of stable Mg|S batteries", without explaining why. They also claim that the sulfur is completely contained within the CNT, but the only evidence given for this is EDS data at one location on the cathode (Fig. S4). Another example of lack of rigor can be found on page 9 lines 45-47 where the authors report higher impedance for TC-S and then state "This suggests that the concentration of dissolved polysulfides in the electrolyte for TC-S is higher compared to that CNT-S with increasing cycle number". There is no further explanation for the connection between higher impedance and dissolved polysulfides.

c. Other corrections:

i. The term "in operando" is incorrect. Please change to "operando". It is grammatically incorrect to say "in operando", see Bañares 2005
https://www.sciencedirect.com/science/article/pii/S0920586104008065

ii. Page 9 line 15 "with respect" repeated

iii. Page 9 line 43 remove "than"

iv. Page 4 line 3. Refers reader to Figure 1b, which doesn't show Raman spectra intensity. Also figure S5 shows Raman shift at a wavelength range not referred to in the text. It also does not show the scale of the Raman spectra, so comparing intensity is futile.

v. Supporting information: colors are incorrect in Figures S1, S5. Figure S5, no description of labels D & G. Figure S8d has the wrong axis label, should be Concentration. Figure S9 has wrong axis label. Should be "weight %" not "weight loss %". Otherwise it would start at zero and increase to 82%.

Reviewer: 2

Comments to the Author

This paper presents the significance of in operando RAMAN and ex-situ UV-Vis spec experiments to probe and investigate in detail the characteristics of two different host cathodes, CNT and TC during galvanostatic cycling. For instance the through operando Raman, at a discharge voltage of 1.3V, the authors observed band splitting at 153 cm-1 and 219 cm-1 which were attributed to the confinement of higher order polysulfides in CNT. The UV-Vis spectroscopy also support this showing less polysulfide dissolution in the electrolyte. As a result of this ideal chemistry (perhaps as the suggest due to the interaction between the Sulfur of the metal polysulfide and the main functional groups on the host cathode), better battery performance was observed with higher capacities (at diff. C-rates) and lower overpotentials in the presence of CNT (when compared to TC). Such in-depth experiments are very useful and important in order understand the different chemistry and performances observed in the Mg-S battery in the presence of various porous electrodes. The authors have done a thorough job of understanding the battery chemistry at different discharge voltages using the in operando and ex situ techniques. This manuscript should be accepted for publication as is.

Author's Response to Peer Review Comments:

Non-scientific correction

1. Title: Using acronyms in title is discouraged. Please spell out all acronyms in the title of the manuscript and Supporting Information.

Reply: As per the editorial board suggestion, we have spelled out all acronyms in the title of the revised manuscript and in the revised supporting information.

2. TOC Graphic: Please resize per journal guidelines (2 in x 2 in) and move to the correct position (on the same page as the abstract).

Reply: As per the editorial board suggestion, we have resized the TOC graphic to 2 in x 2 in and moved it to the abstract page in the revised manuscript.

3. References: In both the main file and the supporting information, fix the style of all references to use JPCL formatting (check all references carefully). ***JPC Letters reference formatting requires that journal references should contain: () around numbers, author names, article title (titles entirely in title case or entirely in lower case), abbreviated journal title (italicized), year (bolded), volume (italicized), and pages (first-last). Book references should contain author names, book title (in the same pattern), publisher, city, and year.

Reply: As per the editorial board suggestion, we have formatted all the references according to the journal in the corrected manuscript.

Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: This paper is probably publishable, but major revision is needed; I do not need to see future revisions.

Comments:

1. Major advance of the paper:

The authors present findings from experiments using carbon nanotubes (CNT) as a cathode material for Mg-S batteries. CNT-based cathodes show improved cyclability, reduced overpotentials, and less polysulfide formation (verified with UV-vis absorption spectroscopy). This performance is compared with literature and shown to be an improvement of the state of the art (see Figure S12)

2. The immediate significance of this advance:

The synthesis method of CNT-S cathodes is reported along with improved cycling performance.

Reply: We thank the reviewer for recommending acceptance of the manuscript after revision and providing valuable suggestions to improve the manuscript.

3. Technical suggestions:

a. The authors report operando Raman spectra of the CNT-sulfur cathode during cycling as evidence of polysulfide confinement in CNTs. For example, on page 6 the authors claim "The bands at 153 cm^{-1} and 219 cm^{-1} are attributed to the presence of higher order polysulfides which confirms the confinement of higher order polysulfides inside the carbon nanotubes of CNT-S cathode". While the reduced PS concentration seen in the UV-vis measurements indicate improved confinement, I do not believe the Raman spectra demonstrates this, at least not in the way the authors claim. The Raman spectra shown agrees well with other Raman measurements of dissolved polysulfides in the literature (For example, liquid-phase Raman spectra of polysulfides are reported in "Raman Spectroscopy Study of the Reaction between Sodium Sulfide or Disulfide and Sulfur: Identity of the Species Formed in Solid and Liquid Phases" https://pubs.acs.org/doi/pdf/10.1021/ic9900096, and operando measurements show similar results in "In Situ Raman Spectroscopy of Sulfur Speciation in Lithium−Sulfur Batteries" https://pubs.acs.org/doi/pdf/10.1021/am5072942.). EDS measurements report at least 6% sulfur outside of the CNT even after repeated washing, and it is likely that this external sulfur is largely responsible for the Raman results.

Reply: The present study demonstrates the intermediate polysulfide confinement mechanism of Mg|S battery using two different host for sulfur viz. CNT and TC. We found that the polysulfides confinement is more effective in case of CNT-S by using operando Raman spectroscopy. The extent of intermediate polysulfides dissolution in two different sulfur host is further confirmed using ex-situ UV-Vis spectroscopy which indicates, higher polysulfides dissolution in case of TC-S cathode. Our result matches well with previously published literature [1-3], where authors have used in-situ/operando Raman to study the polysulfides dissolution.

At OCV, both cathodes i.e., TC-S and CNT-S display Raman bands at 157 cm^{-1}, 223 cm^{-1} and 475 cm^{-1} due to presence of sulfur (Figure 3). This matches well with the Raman spectra of the elemental sulfur (as in Figure 1b). During discharge, at 1.3 V, it is observed that in case of CNT-S, additional humps appear at 153 cm^{-1} and 219 cm^{-1} (Figure 3, zoomed plots). This is attributed to the formation of higher order polysulfides. The occurrence of these humps in case of CNT-S suggests that the formed higher order polysulfides are getting confined within the carbon nanotubes. We do not think that these humps are due to the presence of sulfur (6 % sulfur, in case of CNT-S from EDS measurement) residing outside. If this was the proposition, then similar humps would have also appeared in the case of TC-S. In TC-S, the intensities would have been larger, as all the sulfur is spread throughout the open matrix (as seen in SEM, Figure 2c). So, we strongly feel that the CNT is more effective in confining S than TC and this jointly supported by operando Raman and ex-situ UV-VIS studies.

b. I also found the paper lacking in rigor. For example, on page 2 the authors state that polysulfide dissolution is an "even greater challenge impeding the success of Mg|S batteries" and become "even more important for the development of stable Mg|S batteries", without explaining why. They also claim that the sulfur is completely contained within the CNT, but the only evidence given for this is EDS data at one location on the cathode (Fig. S4). Another example of lack of rigor can be found on page 9 lines 45-47 where the authors report higher impedance for TC-S and then state "This suggests that the concentration of dissolved polysulfides in the electrolyte for TC-S is higher compared to that CNT-S with increasing cycle number". There is no further explanation for the connection between higher impedance and dissolved polysulfides.

Reply: We have corrected the statements in the revised manuscript. Polysulfide dissolution is a major concern in all metal sulfur battery. Like Li-S and Na-S system, various intermediate polysulfides formation takes place during the discharge and charge. This results in low utilization of active sulfur, poor cycle life and low coulombic efficiency. To obtain a stable Mg-S battery cycling, the problem of intermediate polysulfides dissolution needs to be tackled effectively.

Apart from the EDS measurement, we have also performed XRD and Raman spectroscopy studies (Figure 2a & b) to confirm the successful confinement of sulfur into the closed matrix of CNT. In the case of CNT-S cathode, the XRD peaks due to sulfur is less prominent. This is also supported by Raman spectroscopy data. In comparison, the XRD data for TC-S cathode shows more prominent peaks thus, confirming that it is less effective in confining sulfur than the CNT host.

Explanation for page-9 lines 45-47: It is mentioned in the literature ref [4], the solution resistance of the sulfur cell grows gradually with increasing the cycle number. It can be attributed to the increase in the concentration of dissolved polysulfides in the electrolyte, leading to an increase in the viscosity of the electrolyte and a decrease of the electrolyte conductivity. In the present work, mechanism of polysulfides dissolution is carried out by using two different sulfur host (e.g., CNT, TC). In the case of CNT-S cathode sulfur and intermediate polysulfides are confined inside the MWCNT which is confirmed via operando Raman spectroscopy. As a result, the dissolution of higher order polysulfides is less in the case of CNC-S cathode compared to TC-S cathode. Due to high rate of dissolution, the polysulfides concentration is more in the Mg-S cell with TC-S cathode which increases the viscosity of the electrolyte and resulting in high impedance value for TC-S compared to that CNT-S. We have added the explanation in the revised manuscript.

c. Other corrections:

i. The term “in operando” is incorrect. Please change to “operando”. It is grammatically incorrect to say “in operando”, see Bañares 2005 https://www.sciencedirect.com/science/article/pii/S0920586104008065

Reply: We have replaced “in operando” with “operando” in the revised manuscript.

ii. Page 9 line 15 “with respect” repeated

Reply: We have corrected the error in the revised manuscript.

iii. Page 9 line 43 remove “than”

Reply: We have corrected the error in the revised manuscript.

iv. Page 4 line 3. Refers reader to Figure 1b, which doesn’t show Raman spectra intensity. Also figure S5 shows Raman shift at a wavelength range not referred to in the text. It also does not show the scale of the Raman spectra, so comparing intensity is futile.

Reply: We appreciate this point raised by the reviewer. As per the reviewer’s suggestion we have shown the intensity of the Raman bands on the y-axis for both the cathodes as shown in **Figure 1** below (included in the revised supporting file as Figure S5b). The intensity of Raman bands in case of TC-S is much higher compared to that of CNT-S cathode which confirms that the nanotube is more efficient in confining sulfur than the TC. Figure S5 (S5a in corrected supporting information file) shows the characteristic D and G band in the Raman spectra of pure CNT and TC paper material. We have included the explanation in the revised manuscript.

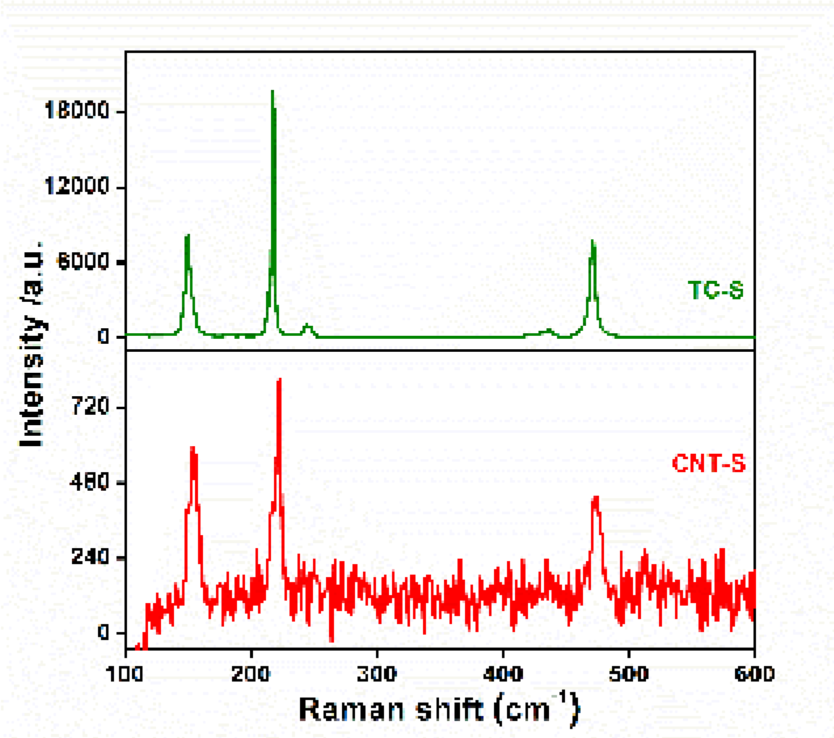

Figure 1: Raman spectra of the CNT-S (red), TC-S (green).

v. Supporting information: colors are incorrect in Figures S1, S5. Figure S5, no description of labels D & G. Figure S8d has the wrong axis label, should be Concentration. Figure S9 has wrong axis label. Should be "weight %" not "weight loss %". Otherwise it would start at zero and increase to 82%.

Reply: As per reviewer's suggestions, we have corrected all the figures in the revised supporting information. The description for D &G bands is also added in the figure S5 in the revised supporting information file.

Reviewer: 2

Recommendation: This paper represents a significant new contribution and should be published as is.

Comments:

This paper presents the significance of in operando RAMAN and ex-situ UV-Vis spec experiments to probe and investigate in detail the characteristics of two different host cathodes, CNT and TC during galvanostatic cycling. For instance, the through operando Raman, at a discharge voltage of 1.3V, the authors observed band splitting at 153 cm-1 and 219 cm-1 which were attributed to the confinement of higher order polysulfides in CNT. The UV-Vis spectroscopy also supports this showing less polysulfide dissolution in the electrolyte. As a result of this ideal chemistry (perhaps as the suggest due to the interaction between the Sulfur of the metal polysulfide and the main functional groups on the host cathode), better battery performance was observed with higher capacities (at diff. C-rates) and lower overpotentials in the presence of CNT (when compared to TC). Such in-depth experiments are very useful and important in order understand the different chemistry and performances observed in the Mg-S battery in the presence of various porous electrodes. The authors have done a thorough job of understanding the battery chemistry at different discharge voltages using the in operando and ex situ techniques. This manuscript should be accepted for publication as is.

Reply: We thank the reviewers for acknowledging the importance of the manuscript in understanding the mechanistic of Mg|S battery chemistry using operando Raman and ex-situ UV-Vis spectroscopy and accepting for publication in the Journal of Physical Chemistry Letters.

References:

(1) Yeon, J.-T.; Jang, J.-Y.; Han, J.-G.; Cho, J.; Lee, K. T.; Choi, N.-S. Raman Spectroscopic and X-Ray Diffraction Studies of Sulfur Composite Electrodes during Discharge and Charge. *J. Electrochem. Soc.* **2012**, *159* (8), A1308–A1314.

(2) Hagen, M.; Schiffels, P.; Hammer, M.; Dörfler, S.; Tübke, J.; Hoffmann, M. J.; Althues, H.; Kaskel, S. In-Situ Raman Investigation of Polysulfide Formation in Li-S Cells. *J. Electrochem. Soc.* **2013**, *160* (8), A1205–A1214.

(3) Diao, Y.; Xie, K.; Xiong, S.; Hong, X. Insights into Li-S Battery Cathode Capacity Fading Mechanisms: Irreversible Oxidation of Active Mass during Cycling. *J. Electrochem. Soc.* **2012**, *159* (11), A1816–A1821.

(4) Kazazi, M.; Vaezi, M. R.; Kazemzadeh, A. Enhanced Rate Performance of Polypyrrole-Coated Sulfur/MWCNT Cathode Material: A Kinetic Study by Electrochemical Impedance Spectroscopy. *Ionics (Kiel).* **2014**, *20* (5), 635–643.

jz-2021-03958h.R2

Name: Peer Review Information for "Probing the Polysulfide Confinement in Two Different Sulfur Host for Mg|S Battery Employing Operando Raman and Ex situ UV-Visible Spectroscopy"

Second Round of Reviewer Comments

Reviewer: 1

Comments to the Author

The authors have addressed all but one of my comments. The claim that the peaks shown in Fig 3a are due to "confined" polysulfides lacks evidence. The authors can rightly claim that there is a lower concentration of dissolved polysulfides (as this is corroborated by UV absorption measurements), and by inference claim higher confinement. But the authors make no spectroscopic argument for how their Raman measurements prove the PS peaks seen in Fig 3a are from "confined" PS species. How would the measurement differentiate between PS species outside of CNT (dissolved) and those within CNT? Further, the 1.3V Raman signals are very weak and the high level of noise may mask similar peaks (153cm-1 and 219cm-1) in the TC-S spectra. While the conclusions of the paper are still supported, I still feel the authors must be more precise in their interpretation of the Raman results.

Author's Response to Peer Review Comments:

Response to Reviewer's Comment

Reviewer 1

Recommendation: This paper is publishable subject to minor revisions noted. Further review is not needed.

Reply: We thank the reviewer for the positive comments and granting the acceptance of the manuscript.

Comments:
The authors have addressed all but one of my comments. The claim that the peaks shown in Fig 3a are due to "confined" polysulfides lacks evidence. The authors can rightly claim that there is a lower concentration of dissolved polysulfides (as this is corroborated by UV absorption measurements), and by inference claim higher confinement. But the authors make no spectroscopic argument for how their Raman measurements prove the PS peaks seen in Fig 3a are from "confined" PS species. How would the measurement differentiate between PS species outside of CNT (dissolved) and those within CNT? Further, the 1.3V Raman signals are very weak and the high level of noise may mask similar peaks (153 cm^{-1} and 219 cm^{-1}) in the TC-S spectra. While the conclusions of the paper are still supported, I still feel the authors must be more precise in their interpretation of the Raman results.

Reply: The present study demonstrates the intermediate polysulfide confinement mechanism of Mg-S battery using two different host for sulfur viz. CNT and TC. We found that the polysulfides dissolution is lower in case of CNT-S compared to TC using experimental methods including ex-situ UV-VIS and operando Raman spectroscopy.

The operando Raman spectra for both the cathodes at OCV shows Raman bands at 157 cm^{-1}, 223 cm^{-1} and 475 cm^{-1} due to presence of sulfur (Figure 3). This matches well with the Raman spectra of the CNT-S, TC-S and elemental sulfur (as shown in Figure 1b). Following discharge to 1.3 V, it is observed that in the case of CNT-S, additional humps appear at 153 cm^{-1} and 219 cm^{-1} (Figure 3a, enlarge area). This is attributed to the higher order polysulfides. As the Raman measurement here has been done operando, there is an uncertainty in the exact ascertaining of the origin of such Raman signals. In the context of the methodology adopted here, it will be hard to differentiate, whether the polysulfides are confined inside CNT or residing at the interface of the liquid electrolyte and the S-cathode. The occurrence of these humps only in case of CNT-S strongly suggests that the concentration of polysulfides is higher, which can be due to a combination of polysulfides residing inside CNT and those residing in the liquid electrolyte in the immediate vicinity of the S-cathode. The absence of such humps near 153 cm^{-1} and 219 cm^{-1} in TC-S, strongly suggests higher dissolution in case of TC. Unlike CNT, the TC is not as efficient in confining the higher order polysulfides within it nor restraining substantial amount of polysulfides near to the S-cathode. As the point raised by the referee is an important one, the authors plan to take up in future, such detailed studies using complementary operando methods. Due to technical constraints, these are not feasible in the present time and hence, are outside the scope of this manuscript.

Additionally, the humps observed near 153 cm^{-1} and 219 cm^{-1} are not noise. They are also observed at discharge voltage 0.8 V in the case of CNT-S cathode as shown in Figure 1 below (blue curve in the expanded plot). This result suggested that the humps at 153 cm^{-1} and 219 cm^{-1} (at discharge voltage 1.3 V and 0.8 V) can be due to a combination of polysulfides confined inside CNT and those residing in the liquid electrolyte in the immediate vicinity of the S-cathode. These are absent in the case of TC-S cathode.

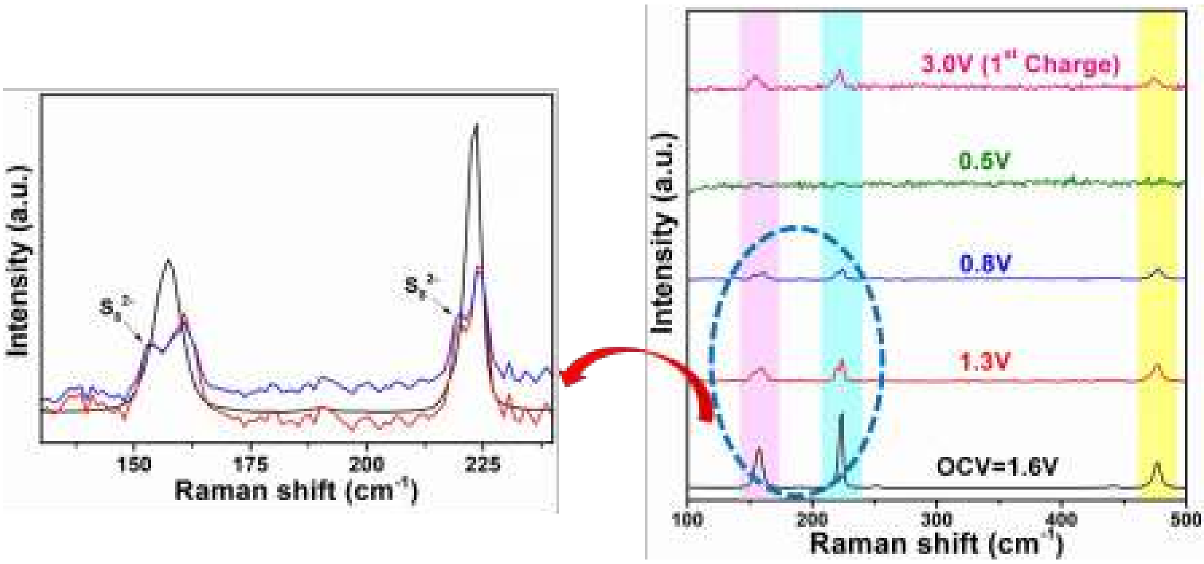

Figure 1: *Operando* Raman spectra of Mg|S cell at different discharge voltages using CNT-S as the cathode. Magnified area shows Raman spectra at 0.8 V (blue), 1.3 V (red) and OCV (black).