

Response to comments from Shi and Atrens on the paper “Observations of the galvanostatic dissolution of pure magnesium”

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Abstract:

A consolidated response is made here to address the comments of Shi and Atrens concerning the manuscript “Observations of the galvanostatic dissolution of pure magnesium”. We provide discussion to indicate that the claims made by Shi and Atrens are invalid from an electrochemical and logical perspective, and therefore there is no basis for Shi and Atrens claim that our work provides evidence for Mg⁺.

Keywords: A: magnesium, B: galvanostatic, C: anodic dissolution.

Shi and Atrens have formulated a rather complex commentary on our manuscript, to which rather than respond to isolated aspects of their comments, some overall discussion is given, followed by individual points to address the incorrect assumptions made by them. We feel that any additional data in our response is not warranted, since we emphasise that comments by Shi and Atrens are not peer-reviewed, and hence have not been assessed independently for correctness. Further, we stand by the raw results in our work (Observations of the galvanostatic dissolution of pure magnesium), the basis of which was to provide a first 'real time' reconciliation of dissolution of magnesium. Atrens and co-workers purport the existence of univalent Mg, and the aim of our paper was to broaden the discussion. It is logical for one to reconcile dissolution with current, as we did, and we have given all the raw data and videos – leaving no doubt as to the experimental validity (discussed further below). We are however grateful for the opportunity to indicate that a minor correction/clarification to our work, which was an obvious gaffe by a 'division by two' error (which is obvious in the paper as the raw data is all given). What was done in the paper is the Charge (C) values reported in Table 1 (and hence Figure 5) are all exactly twice what they should be (because the volume of the wedge is half the volume of a rectangular prism). The factor of two error propagated when the division was not carried from spreadsheet (which was used for data interpretation and discussion) to plotting (via Origin). A division of 2 error is by no means a reflection of misleading electrochemistry, and reflects in now way on the electrochemical interpretations (its simply, a division by 2 error in reporting). In fact, its unrelated to electrochemistry, and changes none of the assertions in the paper in any way, shape or form. As such, our reported charge of 145C corresponding to $n=2$ for dissolution at open circuit should be $145/2$ (this division by a factor of 2 can be applied to all the charge values). This is a simple calculation that any reader can make using Faraday's law – and they will validate the data themselves, which can be logically retrieved from the sample geometry given, and times to dissolution given in the paper (and videos). The key assertions from the work are that the apparent valence varies with the current applied, and that the reconciliation of dissolution in real time, with applied current, is suggestive that the Mg^+ theory is not applicable. We encourage others to reproduce the data (as we did ourselves prior to our response) and believe that others will find: a) Variation in apparent valency with applied current, b) Excellent agreement with Mg^{2+} at high currents. These are two things worthy of reporting.

The discussion from Shi and Atrens is suggestive that they are not open to the consideration of theories alternative to the univalent Mg model, resulting in irrational responses to papers that may conflict with this view. Shi and Atrens

claim that our experimental results demonstrate the existence of the Mg^+ ion in aqueous solution. This is only after they have used an invalid divisor to manipulate the raw data. Whilst the unipositive theory of Atrens may explain some empirical phenomena, it does not mean that it is correct, and it certainly is in growing conflict with emerging works of multiple independent groups using a variety of analytical methods [1-5], not to mention counter intuitive to centuries of research into the chemistry and electrochemistry of magnesium and its compounds. To our knowledge no one has yet managed to isolate any compounds containing Mg^+ , nor has any spectroscopic data ever been published which confirms even the transient appearance of such a species; this is important to note, since Atrens is claiming our data is evidence for Mg^+ . In the field of corrosion research, a theory based on the existence of Mg^+ , with no reasonable proof of its existence, is routinely quoted while ignoring some other more plausible explanations of the so-called negative difference effect (NDE). Atrens has published approximately 70 papers quoting the existence of univalent Mg (24 in *Corrosion Science*) without *any* of evidence for the existence of univalent Mg. Proponents of the Mg^+ theory also readily fail to assess the significant prior and early works in the area, which refute the existence of Mg^+ and provide alternative explanations [7-10].

Before we can invalidate the comments by Shi and Atrens, we need to draw attention to their description of the Mg^+ mechanism of corrosion, the discussion of which invokes the unusual concept of “self-corrosion” as an important factor in causing Mg anode weight loss during an *applied anodic current*. It is not immediately obvious from their comments what exactly they mean by the phrase “self -corrosion”. Our interpretation is that the self-corrosion takes the form of a significant cathodic current (I_c) persisting under anodic polarisation, so that the applied current (I_{appl}) is given by:

$$I_{\text{appl}} = I_a - I_c \quad (1)$$

where I_a is the anodic current. Self-corrosion appears to be at odds with the Mg^+ model of anodic dissolution. It should be noted that the following empirically derived relationship quoted in the Atrens commentary,

$$2(N_{\text{Mg}} - N_{\text{H}}) = N_e \quad (2)$$

where N_{Mg} and N_{H} are the moles of Mg^{2+} released and H_2 evolved respectively per unit time per unit area and N_e is the moles of electrons supplied by external current per unit time per unit area, is simply a statement of equation (1), when it is assumed that Mg becomes oxidised directly to Mg^{2+} ions and that hydrogen evolution occurs via a cathodic reaction. Therefore, a theory involving a Mg^+ intermediate is not required to explain this relationship as it

can more simply be explained by cathodic hydrogen evolution persisting at potentials significantly more positive than open circuit.

In fact, this concept of concurrent “self-corrosion” and Mg dissolution by a Mg^+ intermediate, invoked by Shi and Atrens, is what we can only interpret as their justification to take our data and divide it by the data for dissolution at open-circuit (which is done at the very commencement of the comments from Shi and Atrens). After doing so, they change the whole interpretation of our work in a totally invalid manner. Let us consider corrosion at open-circuit. Under such conditions, the anodes and cathodes are both on the electrode surface, in close proximity, free from any applied polarisation. Under anodic polarisation the electrons resulting from the anodic dissolution reaction either go to a local cathodic reaction or through the wire to the potentiostat. The latest incarnation of the numerous theories by Atrens is discussed in terms of an Mg^+ mechanism and the subsequent chemical reaction of Mg^+ (with water) to form Mg^{2+} and hydrogen gas; where it is also quoted that self-corrosion is more important than the applied current density in causing weight loss throughout the anodic polarisation curve.

- If self-corrosion is in operation, then one must ask whereabouts is the cathode?
- If a cathode exists, it must be on the galvanostatically polarised anode sample (and if there is a cathode present on the sample, then the cathodic reaction must be hydrogen evolution).
- If the cathode were on the anodically polarised sample, then this would negate the Atrens unipositive theory, since the hydrogen evolved would be from a cathodic reaction, and NOT from the chemical reaction of Mg^+ with water to form Mg^{2+} . This is the basis for a major (self) contradiction and invalidates the whole of the commentary of Shi and Atrens (which is incidentally – wholly unrelated to our original paper).

We don't believe that this is actually the forum to debate the work of Shi and Atrens, which is best done by a broader revisiting by interested readers in the wider literature, who we believe can use their own interpretation [1-12]. However, the comments from Shi and Atrens are both self-contradictory and flawed. The evolution of the unipositive Mg theories reported by Atrens was recently critiqued by Frankel et al [4] in a paper that also presented direct evidence to refute the existence of Mg^+ as theorised by Atrens, from completely independent tests, and we direct the readership to this recent manuscript. The notion that the cathodic reaction is catalyzed by Mg dissolution as outlined by Frankel [4], is consistent with the classic works noting enhanced ‘reducing ability’ [7], but also elegantly shown by SVET measurements [11].

Shi and Atrens discussion of our data appears founded on the notion that cathodes exist on the anodically polarised surface (which is the case at OCP) and that self-corrosion is a significant factor - meaning the assumption that the applied galvanostatic current, $I_{\text{applied}} = I_a$ (rate of partial anodic reaction) is incorrect and there will be an appreciable I_c (rate of partial cathodic reaction – *cathodic* hydrogen evolution) to be taken into account. Where then does this then leave the Mg^+ argument, particularly when nobody has ever isolated the Mg^+ compound?

It is difficult for one to reasonably sanction the use of two completely contradictory theories to support the notion of Mg^+ for which there is no evidence in our work. Based on this, the comments from Shi and Atrens are a collection of comments that cannot merit a logical response and cannot be considered to be credible, nor really related to our paper. This is especially alarming given the fact that the unipositive theory has permeated through the literature, and its proponents are also using the unipositive theory as a means for making second order interpretations of alloy corrosion, all of which can only be considered irrational until isolation of the Mg^+ compound has occurred. We believe the original outcomes of our results still stand. Our key findings are that the apparent valency is changing with applied current, as is the charge to dissolution. It is this variation that is interesting and is at odds with the unipositive theory, which is further outlined in [4].

Response to other claims in the commentary by Shi and Atrens

Comment: There are claims by Shi and Atrens that the data is “unclear and contradictory”

Response: This is a completely subjective view and the authors made no attempt to reproduce the data. We feel significant experimental detail is given, with significant raw data. We encourage authors to reproduce the data at the highest current densities, which is the most compelling evidence herein against unipositive Mg, and they will see for themselves that the results are highly reproducible.

Comment: Kirkland et al ignored prior studies by Shi et al.

Response: There are no other prior studies by Shi et al. (or anyone) in the reconciliation of dissolution in real time via video imaging. As such, there is no logical reason to cite unrelated works. The short communication was focused on the delivery of new data.

Comment: It is not clear if Kirkland et al applied a constant current or constant current density

Response: This is an unusual comment, as the paper clearly includes Figure 4 (the applied current density as a function of the percentage of specimen dissolved during galvanostatic polarisation).

Comment: The specimen area does not agree

Response: The calculation by Shi and Atrens is incorrect. The sample is exposed as a 3D entity. The surface area includes ALL sides of the wedge. The reported specimen area is correct.

Comment: Comments regarding reproducibility and experimental details.

Response: The comments from Shi and Atrens give the false impression that each experiment was only conducted once. This is not the case, the reported values are plotted with the relevant error bars and scatter, and tabulated data is average values. The comments regarding variation from sample to sample because of grinding with 2000 grit we believe are irrelevant in the context of the findings. Such variations would have been consistent between replicate samples, and surface effects tend to become less relevant when dissolving a volume. The findings can be very well reproduced, irrespective of the whether the surface is ground to 2000 grit, 1200 grit, or 4000 grit. The comments from Shi and Atrens also give the false impression that the reporting does not allow for results to be reproduced, however Shi and Atrens made no such attempt to reproduce the data and hence their claims have no basis. The data at high current densities, which is the most compelling evidence herein against unipositive Mg, is irrefutably reproducible based on our numerous tests. Furthermore, the recent work of Frankel [4] also adds to the debate in that when researchers go looking for unipositive Mg, the data indicates that its existence based on the theory of Atrens is not possible, as the amount of hydrogen produced for a given charge decreases with increasing applied current.

Comment: Discussion regarding the two independent studies of McMurray et al. [2], and Swiatkowska et al. [1].

Response: From the outset we believe it is wholly inappropriate to use the non-peer reviewed vessel of a comments communication to discuss work in other independent studies for which the authors have no reasonable means of rebuttal. We will not entertain such comments, other than make the following statement. We mentioned the work of Williams and McMurray et al [2] and Swiatkowska et al [1] to indicate instances of when other independent groups have by real-time that experiments indicated that unipositive Mg did not prevail. The Williams and McMurray paper [2] discussed in this section reports on the localised corrosion behaviour of magnesium freely corroding in chloride solution, which does not require the use of the unipositive Mg model to explain. Nevertheless, the interpretation of the results as being consistent with a mechanism whereby anodic dissolution of Mg to Mg⁺ at the perimeter of a

circular corroded region couples with cathodic hydrogen evolution located within its centre, merits some comment. In a subsequent paper, [6], Williams et al. compared the hydrogen evolution rate calculated from numerical integration of *cathodic* localised current density values, with a rate obtained by measuring the time-dependent volume of hydrogen evolved for Mg immersed in 5% w/v NaCl (aq). The close agreement of integrated SVET data with the measured H₂ evolution rate observed over the first hour of immersion could only have arisen if hydrogen evolution was solely derived from a cathodic reaction. For the Mg⁺ corrosion model, integration of cathodic current density values would have only accounted for half of the measured H₂, and as a consequence is inconsistent with these empirical findings. In our paper, we did not interpret the results of McMurray et al [2] and Swiatkowska et al [1] other than to repeat their conclusions that there was no evidence for unipositive Mg. It can also now be noted that the recent work of Frankel et al [4] can be added to this list, as can the recent work of Souto et al [5] and Lee et al [12]. We also remind readers that no one has yet managed to isolate any compounds containing Mg⁺, nor has any spectroscopic data ever been published which confirms even the transient appearance of such a species.

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