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Response to "unsupported claims of ultrafast charging of Li-ion batteries"

Rechargeable batteries, and energy storage in general, have become a focal point of the future energy landscape as it will play a critical role in clean energy generation and use. The demands of these new applications will require significant breakthroughs as well as rethinking of current ideas regarding battery performance and design. In a recent Letter to Nature on "Battery materials for ultrafast charging and discharging" we demonstrated that it is possible to create active cathode materials for Li batteries with extreme rate capability [1]. In their Comment Zaghib et al. [2] (hereafter referred to as ZGMJ) dispute what they believe to be claims made by us in Ref. [1] and refer to it as a "deceptive" paper. While ZGMJ make several useful Comments which should help battery researchers focus on important challenges to create high rate batteries, we regret the harsh words used by our colleagues and will point out that several of their statements are incorrect, and some, regrettably, misrepresent what is actually stated in the Letter. We encourage the reader to read the original Letter [1] in order to assess the validity of the claims made by ZGMJ. The Letter [1] deals with the performance of an active cathode material as tested in half cells and demonstrates both fast charging and discharging of the material. Unlike what the title of the Comment by ZGMJ states, the terminology "Li-ion batteries" is never used in the paper.

In Ref. [1] we argue on the basis of the calculated Li–Fe–P–O phase diagram that creating Fe and P deficiency in a 2/1 ratio in the starting materials can create $LiFePO_4$ together with a pyrophosphate-like second-phase component. We show that this material has extreme high rate capability, and conclude the paper by speculating on the potential applications and problems for batteries that could be charged at very high rates. Besides the smaller Comments ZGMJ make about our work in Ref. [1], we detect in the Comment four basic criticisms/Comments: (1) They argue that we do not give any evidence for high charge rate capability of the modified material and that this is deceptive as – according to them – high charge rate of a material does not follow from high discharge rate. (2) They argue that the caption to Fig. 3 in Ref. [1] is misleading, (3) They offer an alternative explanation for the presence of Fe^{3+}, and (4) They argue that carbon coating – a technology on which several of the authors of the ZGMJ Comment have performed extensive work – is responsible for the high rate performance. In addition to these four basic Comments we will deal with the smaller points separately. We will thereby clarify that our modified $LiFePO_4$ is (i) capable of very high rate charging, (ii) that this was clear in the original Letter, and (iii) that it is not "implausible" – as stated by the authors, to construct batteries with extreme high charge rate capability.

1. High charge/discharge rate

The objective of our work in Ref. [1] was to verify the theoretical work [3,4] that Li mobility in $LiFePO_4$ is extremely high and therefore not rate limiting for high charge or discharge behavior. Our results confirm that theoretical prediction and show that this active cathode material will not be rate limiting, even under very high rates of charge and discharge. We first of all point out for the reader that experiments in our work are performed on half cells with a metallic Li anode. Unlike what ZGMJ state we never discuss the issues with Li-ion cells in which the anode is carbon. Such experiments on half-cells are common in the literature and appropriate if one wants to isolate the rate limitations of the active cathode material.

We chose to present discharge experiments as we believe that they are more controlled than charge experiments. Discharge experiments show the energy that can be released by the material under high rate. High rate charge experiments can suffer from energy dissipative process that would overestimate the capacity of the cell. However, the ability to charge fast is clearly and directly shown in Fig. 3b of Ref. [1] which gives cycling capacities for the cell in which both charging and discharging is at the specified high rate, a fact that ZGMJ regrettably misrepresent in their Comment. Clearly, these high cycling capacities would not be possible if the material was incapable of charging fast. Voltage profiles for the charge and discharge in the cycling test used to generate the data in Fig. 3b and Fig. 4 in Ref. [1] are plotted in Fig. 1 of this paper. Furthermore, while ZGMJ do not dispute our results indicating extremely high discharge rate capability, they argue that charge and discharge rate capability are asymmetric and hence, our results would not necessarily justify a claim for high charge rate capability. We disagree. Unlike what ZGMJ claim, active materials show only very limited asymmetry in the rate at which they can be lithiated or delithiated, and asymmetry of the active materials is only related to non-linearity of the Li diffusion constant with concentration or to asymmetric nucleation kinetics in first order lithiation/delithiation phase transitions [5,6]. For example, Srinivasan and Newman [6] showed that there was some asymmetric behavior in $LiFePO_4$ electrode but with the charge actually being faster than the discharge in $LiFePO_4$. Hence, there was no "deception" in Ref. [1] by only showing discharge results in Fig. 3a of Ref. [1].

The materials tested to obtain the discharge data in Fig. 3a of Ref. [1] are indeed capable of fast charging: Fig. 1 of this paper shows both the charge and discharge profiles from the data in Fig. 3b and Fig. 4 in Ref. [1]. The rate tests up to 60 C were performed on electrodes with 15 wt% carbon, and the 200 C and 400 C tests were performed with 65 wt% carbon in the electrode. Fig. 1a–e clearly shows that the fast discharge ability of this material is matched by

0378-7753/$ – see front matter
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a fast charge capability. In contrast to the statement made by ZGMJ there is no significant asymmetry in the charging and discharging of the active material.

We note that the 400 C charge rate (Fig. 1d) corresponds to about 9 s for a full charge (based on full theoretical capacity). Hence, unlike what ZGMJ state in their Comment a 9 s charge of this material is not "impossible".

It is worthwhile pointing out that the points made by ZGMJ regarding asymmetry in charging and discharging do not relate to the active materials, but are relevant for a conventional Li-ion cell with a carbon anode, an issue not addressed by the work in our paper [1]. In a Li-ion cell the limited charge capability is unrelated to the release rate of the cathode material, but is due to the low potential of the carbon anode where any significant overpotential would

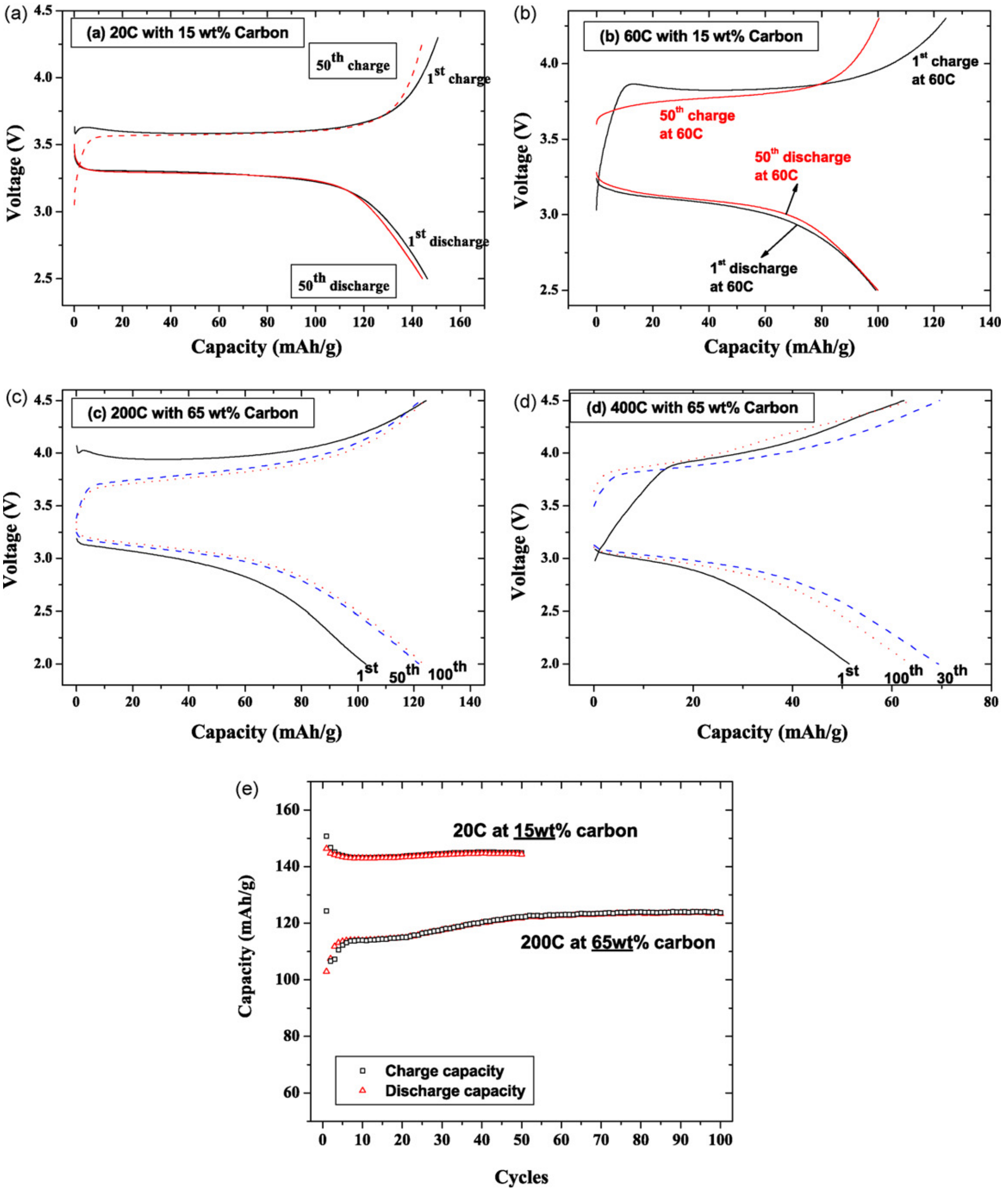

Fig. 1. Charge and discharge voltage profile at *n*C for $LiFe_{0.9}P_{0.95}O_{4-\delta}$. (a) Charge and discharge voltage profile at 20 C for the 1st and 50th cycle. The cell was charged at 20 C and discharged at 20 C with a 1 min open-circuit rest at the end of each charge/discharge cycle. The voltage window was 2.5–4.3 V and the loading density was 3.6 mg cm^{-2}. The formulation of electrode was 80(active), 15(carbon), and 5(binder) in wt%. (b) Charge and discharge voltage profile at 60 C for the 1st and 50th cycle. The cell was charged at 60 C and discharged at 60 C with a 1 min open-circuit rest at the end of each charge/discharge cycle. The voltage window was 2.5–4.3 V and the loading density was 2.71 mg cm^{-2}. The formulation of electrode was 80(active), 15(carbon), and 5(binder) in wt%. (c) Charge and discharge voltage profile at 200 C for the 1st, 50th and 100th cycle. The cell was charged at 200 C and discharged at 200 C with a 1 min open-circuit rest at the end of each charge/discharge cycle. The voltage window was 2.0–4.5 V and the loading density was 2.96 mg cm^{-2}. The formulation of electrode was 30(active), 65(carbon), and 5(binder) in wt%. (d) Charge and discharge voltage profile at 400 C for the 1st, 30th and 100th cycle. The cell was charged at 400 C and discharged at 400 C with a 1 min open-circuit rest at the end of each charge/discharge cycle. The voltage window was 2.0–4.5 V and the loading density was 2.96 mg cm^{-2}. The formulation of electrode was 30(active), 65(carbon), and 5(binder) in wt%. (e) Charge and discharge capacity retention data at 20 C and 200 C. The 20 C data is obtained with the electrode formulation described in Fig. 1(a) and the 200 C data is obtained from the cells used to obtain the data in Fig. 1(c). Note that the 1st charge capacity is always larger than 1st discharge capacity.

cause Li plating. This problem, while important, is specific to carbon anodes and, unlike what is insinuated by ZGMJ, does not preclude the development of high charge rate Li-ion cells as other, high rate anodes are already available, and continue to form an active area of research.

2. ZGMJ claim that the captions to Fig 3 are misleading

ZGMJ claim that there is "ambiguity" on how the experiments shown in Fig. 3 in Ref. [1] are performed. We regret that the procedure seems ambiguous to these authors, most of them well renowned battery experts. In point (5), the most misleading part of the ZGMJ Comment, the authors construct a set of speculations to erroneously conclude that to obtain the data in Fig. 3b in Ref. [1] "the charge is performed until the current reaches C/60. So that the charge has been performed at the slow rate of C/5, and only the discharge has been performed at the 20 C, 60 C ... up to 400 C rates" Note that this inference is purely that of ZGMJ and not a representation of what is actually stated in the paper. Actually, this rather bold and speculative statement is incorrect and regrettable: **To obtain the data in Fig. 3b of Ref. [1] both charge and discharge were performed at the specified high rate see Fig. 1 in this reply**, as is implied by "full charge–discharge cycles at constant 20 C and 60 C current rates". A 1 min open-circuit rest was used at the end of charge and discharge. We agree that our word choice could have been better, but we disagree with the argument by ZGMJ that this is "deceptive". On the contrary, we believe that their unverified and incorrect statements about our data do a disservice to the discussion regarding the performance of this material. We also point out that loading densities of the electrodes (all specified in the captions) are different in Fig. 3a and 3b in Ref. [1], a factor not taken into account by ZGMJ in their incorrect speculation.

Similarly, we do not agree that there is any ambiguity on how the data in Fig. 3a in Ref. [1] is obtained, as asserted by ZGMJ. When discussing Fig. 3, the main body of the text states "Fig. 3a shows the discharge of the material at various rates after a slow charge and hold at 4.3 V to fully charge the material." That sentence is followed by an explanation to the readers of Nature of what "C-rate" means. Figures in Ref. [1] are clearly marked with the rate under which the discharge is performed and the caption to Fig. 3a states "Discharge rate capability after charging at C/5 and holding at 4.3 V until the current reaches C/60." In addition, the title of Figures is "Discharge rate capability and Capacity Retention ..." Both the caption and the main body of the text clearly state what the electrochemical procedure is: slow charge at C/5, followed by hold at 4.3 V, and then discharge at various rates.

3. Arguments on the Fe^{3+} component in the material

While the points made above should clarify the high charge rate capability of the material, we agree that one can state with less certainty what the composition and origin of the phases in the material are. While we believe this issue is part of the scientific discussion and does not relate to the issue of "deception" claimed by ZGMJ we address it here: While we argue that the Fe^{3+} in our material is likely present as pyrophosphate-like structure, ZGMJ argue that it must be the result of contamination and reaction with water which creates Fe^{3+} in the surface, as they believe that one cannot have Fe^{2+} and Fe^{3+} phases coexist in a phase diagram (see their erroneous statement about our phase diagram in Ref. [1] being wrong). They further argue, based on Eq. (1) in Ref. [2] which assumes the formation of $Li_4P_2O_7$, that no Fe is left to be present in the coating phase. We deal with each of these arguments in turn.

Undoubtedly, exposure to air can extract Li from the surface and thereby create Fe^{3+} as shown by some of the authors of the Comment as well as by others [7,8]. We do not dispute this but argue that Fe^{3+} in our materials is already present in the as-made material. Unlike what the authors argue in their point (2) Fe^{3+} phases can obviously coexist with Fe^{2+} phases in a multi-component phase diagram. Phase coexistence is governed by the law of thermodynamics and there is no law or derivative principle that states that in a multi-phase system, transition metal ions should have the same valence. Hence, the second statement of ZGMJ – stated without reference or supporting principles – that there is "a mistake in the phase diagram presented in the Supplementary Information of Ref. [1]" is wrong. The Li–Fe–P–O phase diagram determined in Ref. [9] not only obeys all thermodynamic principles, but is also consistent with the fact that different valence states of a transition metal ion can coexist under equilibrium conditions, a fact that does not seem to be accepted by ZGMJ (their Point 2). A good example of this is for example the work of Paulsen and Dahn [10] who show through rigorous experimental work how different Mn valence states coexist in different phases under a given atmospheric conditions. In addition, mixed valence in a single compound is well known.

ZGMJ point out (Eq. (1) in Ref. [2]) that if stoichiometric $LiFePO_4$ and $Li_4P_2O_7$ were to form the composition of the sample dictates that no Fe can be present in the pyrophosphate, Eq. (1) in Ref. [2] has several underlying assumptions, which are not valid. The argument made by ZGMJ with Eq. (1) in Ref. [2] only applies if stoichiometric $Li_4P_2O_7$ was formed. But note that in Ref. [1] we never state that $Li_4P_2O_7$ forms nor is there any evidence for it in the samples synthesized at 600 °C and 700 °C. In the ternary phase system there are many more ways to accommodate the off-stoichiometry than given by Eq. (1) of ZGMJ. For example, if the glassy phase can exist in the composition triangle between Li_3PO_4, $Li_4P_2O_7$ and $LiFeP_2O_7$ (see phase diagram in Supplementary Information of Ref. [1]) then all of the off-stoichiometry can be accommodated by this mixed phase. Glass formation in tetrahedral solids such as phosphates and silicates is common, and the references in the Supplementary Information of Ref. [1] on the compositions of Fe-containing pyrophosphate glasses demonstrate that such compositions are possible and likely. Given that there is no indication of a stoichiometric $Li_4P_2O_7$ component in our samples we conclude that there is no evidence to support Eq. (1) of ZGMJ and believe it is more likely that the Fe^{3+} component is present in the pyrophosphate as is typical for glasses in this composition range (see references in the Supplementary Information of Ref. [1]).

We have further evidence that the Fe^{3+} is not present due to surface exposure, but as a direct result of the off-stoichiometry in the starting materials, consistent with the phase diagram in the Supplementary Information in Ref. [1]. Our Mössbauer shifts and splittings for Fe^{3+} are different from those obtained by Yamada and co-workers [7] for exposed $LiFePO_4$. Furthermore, if Fe^{3+} is present because Li is extracted from $LiFePO_4$ due to surface exposure, then electrochemical lithiation of the material restores the loss of lithium [7,11]. After the first discharge, the material should not show much activity below the equilibrium potential (~3.5 V). However, the off-stoichiometric material showed constant capacity, 15–18 mAh g^{-1} in the 2.0–3.2 V window typical for other iron pyrophosphate compounds [12]. (Figure S5 in Supplementary information of Ref. [1]). The stoichiometric material which underwent exactly the same handling typically only shows a few mAh g^{-1} capacity in this voltage range. Ironically, ZGMJ refer to their own work (Ref. [7] in the Comment) on stoichiometric $LiFePO_4$ that there is no pyrophosphate present. Given that we deliberately create the pyrophosphate-like structure exactly by going off-stoichiometric, this argument of ZGMJ seems actually consistent with our findings, rather than contradict it.

In summary, while it is difficult to exactly characterize the second-phase component, there is no evidence for the suggestion of ZGMJ that the balance of the off-stoichiometry is present as stoichiometric $Li_4P_2O_7$. Based on the phase diagram, the spectroscopic information, and the initial discharge characterization we believe that most of the Fe^{3+} component is present in a pyrophosphate component.

4. ZGMJ argue that carbon coating is responsible for the high performance of the material

Hydro-Quebec as the exclusive license holder to the $LiFePO_4$ material developed by Professor Goodenough markets material which is carbon coated to improve its performance. We do not want to argue or dispute the merits of carbon coating as it is well outside of the scope of the main claim of our Nature paper or the ZGMJ Comment that our work is "deceptive". There is little doubt that carbon coating enhances the transport of electrons through the composite cathode and as such is an effective way to reduce polarization. However, others have argued that small particle size is much more determining factor for the rate capability than carbon coating [13]. In addition, several groups have shown that high rate $LiFePO_4$ can be obtained without carbon coating [14–16]. We do not dispute that carbon residue from the precursors will be beneficial for electron delivery to the active material. However, no carbon coated materials have ever achieved the performance that we showed in Ref. [1].

We believe that this addresses the main relevant points made by ZGMJ in the Comment. Several other points, not directly relevant to the claims of fast charging or discharging are made by ZMGJ. As they relate more to the mechanism of the high rate capability, we discuss these separately.

In points 9 and 10 ZGMJ continue to speculate of what the microstructure of our off-stoichiometric material is, based on their own experience with stoichiometric materials. We remind the reader that our microstructure containing the pyrophosphate-like component is deliberately induced by the off-stoichiometry, and in our experiments, is NOT present in stoichiometric material. Hence, we find it regrettable that ZGMJ have chosen to speculate on the nature of the pyrophosphate-like component in the material without adding data, or any attempts to reproduce our work. In particular their claim that "the results displayed in the paper suggest that the $Li_4P_2O_7$ does not coat the particle, but is present as nanoparticles that stick at the surface of the particles like other impurities" seem rather premature and unsupported, given that, as far as we know, they have neither investigated our materials, nor is there any evidence shown in Ref. [1] that "nanoparticles stick at the surface" as surmised by ZGMJ.

In Point 8 ZGMJ argue with our calculation of the Li diffusion constant in Li_XFePO_4, even though this was not the subject of Ref. [1] but presented in earlier work by us [3] and others [4]. ZGMJ state that "the calculation of the diffusion coefficient in Ref. [1] was made on the basis of diffusion in a homogenous solution, which is irrelevant to the case of $LiFePO_4$ since the $LiFePO_4/FePO_4$ system is bi-phasic under normal conditions." This is incorrect, and we urge the reader to consult the original work [3]. Yes, the phase transformation is first order, but this does not imply that Li diffusion is irrelevant. The overall result of lithiation/delithiation is Li mass transport and a material with poor Li mobility would not be able to charge or discharge fast, whatever the mechanism. At this point there is no clear understanding of the process by which $LiFePO_4$ ($FePO_4$) transforms, either in nanoparticles or in large crystals, but high Li mobility is a requirement for any process. Even if lithiation were to be interface controlled (which is not clear at this point) Li cannot instantaneously appear at the interface as it still needs to migrate to the lithiation front. A high Li diffusion constant is a pre-requisite for high rate capability. Even in different models for the phase transformation [17,18] fast diffusion down the tunnels in the *b*-direction of the crystal is important. Statements in the ZGMJ Comment about "percolating modulated structures that are formed in a process similar to spinodal decomposition" are unsupported by any evidence.

ZGMJ state that "The authors in [1] claim to have made $LiFe_{0.9}P_{0.95}O_{4-\delta}$ by creation of an iron:phosphorus deficiency. That is not true: the material is not this solid solution". We find this Comment to be exceedingly misleading. We never state in the paper to have created a solid solution. On the contrary, the paper is very clear about the objective to create a multi-phase mixture. We quote from Ref. [1] (second column, first page) "Our synthesis strategy has been to create an appropriate off-stoichiometry in the starting materials so that the coating constituents phase-separate from $LiFePO_4$ as it forms during the heat treatment, thereby creating the active storage material and coating in a single process." Clearly, we neither claimed nor intended to have made a solid solution, and this incorrect statement by ZGMJ is regrettable.

In Point 12 ZGMJ state "the reason why the authors could discharge at such high rates is due to the 65 wt% carbon: so much carbon is needed to carry the current it transforms the battery into a carbon supercapacitor." ZGMJ state this without any data or reference. This would be a carbon supercapacitor that approximately operates at the same voltage as $LiFePO_4$? Unfortunately for ZGMJ this speculation in their Comment is also incorrect. We tested the electrode mass (carbon + binder in ratios of 93/7 wt% and 94/6 wt%) without the active mass at currents representative of the testing in Ref. [1]. At 72 mA g^{-1} of electrode mass, which corresponds to a very low charge/discharge rate we obtain about 8 mAh capacity per gram of active mass between 4.5 and 2 V. At 8.3 A g^{-1} of electrode mass which is still below the highest charge/discharge rates tested in Ref. [1] the inactive mass (carbon + binder) does not contribute any measurable capacity. Hence, the statement by ZGMJ, presented without any data, is incorrect, and the capacity measured in Ref. [1] can be attributed to the active materials.

We state in the paper: "For an electrochemical cell to deliver energy at high rate, all parts of the Li^+-electron path between the anode and cathode active material have to be capable of sustaining this rate" Hence, we do not disagree with most of what is said in Point 14 of the Comment. These calculations indicate the significant obstacles associated with creating very large high power batteries. We do not disagree, but see these problems as challenges rather than obstacles. We would like to point out that for example, research on novel high rate capable anodes is well under way and cells with LTO [19,20] can already sustain very high charge rate up to 80 C. While LTO may not be the ideal anode material due to its high voltage, other high rate anodes [21–23] are to be developed as a result of the increasing research activity in this field. Hence, batteries that can be charged at very high rate are not as impossible as implied by ZGMJ, but they may require a significant shift in the materials and cell design used in current Li-ion technology.

In conclusion, our claims of an active cathode material that can sustain a very high charge AND discharge rate are supported by data, and in agreement with theoretical analysis of the transport phenomena in $LiFePO_4$. The Comments and speculations made by ZGMJ about statements and testing procedures in Ref. [1] are on multiple occasions incorrect. Though we regret the tone and the factual inaccuracies of the ZGMJ Comment we appreciate the emphasis on the technological challenges that lie ahead for creating safe and stable high rate batteries, and hope that this discussion in both Comments helps in pointing out both the challenges and opportunities for battery research.

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