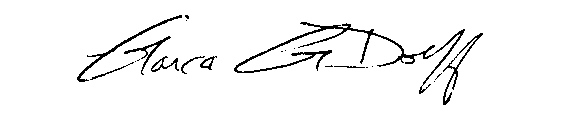
April 5, 2013

Dear Dr. Kinahan,

Here is our revised manuscript. Note that the title has changed based on the request of one reviewer. It is now called “**Characterization of Electrode Materials for Lithium Ion and Sodium Ion Batteries using Synchrotron Radiation Techniques”.** Although it is clear that the referees were somewhat unaware of the unusual format of the journal and the fact that filming is involved, we found many of their comments to be useful, and incorporated many of their suggested changes in the manuscript. We are particularly grateful to reviewers 2 and 3 for clarifications on fluorescence vs. transmission modes in XAS experiments. Based on their inputs, we have removed the discussion of fluorescence mode from the manuscript, as it is not really relevant to the experiments under discussion. Reviewers 2 and 3 also wanted more discussion of the pros and cons of *in situ* vs. *ex situ* experiments. We have now added a paragraph discussing the drawbacks of *ex situ* experiments. A list of the reviewer comments and our responses are appended to this letter. Changes to the manuscript are marked in red. We hope that the revised manuscript is now suitable for publication, and we look forward to scheduling the filming session.

Sincerely,



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**Response to Reviewers' comments:**

*Reviewer #1:*

***Manuscript Summary:***

***The submitted manuscript is a concise description of "Characterization of Electrode Materials for Lithium Ion and Sodium Ion Batteries using Synchrotron Techniques." The paper should be published in JoVE, but the know-how of the manufacture method of an in-situ cell should be explained in detail in the revised paper.***

***Major Concerns:***

***Authors should describe the procedure which makes an in-situ cell in more detail. In addition, they should explain the know-how of the manufacture method of an in-situ cell in detail in the revised paper.***

**Due to space constraints, more written specifics considering the construction of the *in situ* cell cannot be included in the manuscript. However, electrode and cell fabrication is included in the protocol and will be filmed, allowing readers and viewers of the final product to observe these procedures in detail.**

*Reviewer #2:*

***Editorial Comment: This reviewer has requested that a large deal of information be added to your manuscript. Please revise the manuscript according to these comments so that it relays your protocol - along with background information and representative results - as clearly, correctly and effectively as possible. JoVE publications generally have shorter introduction sections and focus primarily on the protocol being demonstrated. We do not expect a thorough discussion of all aspects of the field nor the intricacies of alternative methods.***

***Manuscript Summary:***

***In this manuscript is attempted a report about the required steps needed for the applicability of synchrotron radiation based XRD and XAS on battery materials. Authors provide a brief overview of the techniques but mainly a list of actions required (with bullets) in order to perform these experiment in a synchrotron radiation facility (e.g. preparing the samples, performing measurements, analyzing the data, etc); these are based on their research efforts performed at SSRL beamlines. Some indicative -but already published- results are reviewed and discussed for the purposes of this document.***

***Minor Concerns:***

***In title please change the "Synchrotron Techniques" to "Synchrotron Radiation Techniques"***

**Done.**

***in page 5 line 169-172: The authors mention that the XAS pre-edges arise from dipole forbidden transitions. This is mostly valid for octahedral geometries. For tetrahedral, these transitions are not totally dipole forbidden but mainly are there due to the orbitals hybridization induced by the ligands presence (for example, in 3d metals there is a strong 3d-4p mixing upon tetrahedral geometries; XAS mostly probes that 4p character, thus pre-edge is mostly a dipole allowed transition (1s->4p)). (see for instance F. de Groot et al, J. Phys.: Condens. Matter 21 (2009) 104207)***

**Statement has been modified and reference added.**

***in page 5, line 181: the "a complete picture" statement might be too strong.***

**Statement has been modified.**

***in page 5, line 152-160: the authors could also mention the recent development of high throughput inelastic x-ray scattering setups that allows XAS-like studies on low z elements like C,O, etc. by means of hard x-rays and thus can be suitable for in-situ battery related studies (for instance X. Liu et al., JACS 134, 13708 (2012); Sokaras et al., Rev. Sci. Instrum. 83, 043112 (2012); M. Chen et al, J. Phys. Chem. Lett. 2, 2483 (2011))***

**A paragraph summarizing these points and incorporating these references has been added to the end of the discussion section, where a brief description of where the field is going is included.**

***in page 11, line 365-366: Maybe they could discuss a bit on the influence of the electrode holes -required for transmission measurements- on the battery performance and then on how representative is the probing area (with the holes) compared to the pristine battery.***

**This is covered in the discussion section (p. 15) where we state that results are representative of batteries operating under normal, but not abuse, conditions.**

***in page 11, line 386: please quote the average energy fluctuation.***

**The issue is primarily temperature fluctuations over the course of the experiment. This is now clarified in the sentence.**

***in page 12, line 410: It is clear that from a practical point of view the ex-situ measurements are much easier to perform from various perspectives. However, what seems crucial to discuss is on whether is there a fundamental importance of doing the measurements in situ. I think authors should write a few sentences on this in-situ vs ex-situ (a paragraph or so).***

**We discuss the reason for doing in situ experiments briefly in the Introduction ( “As a result, electrode structural changes can be observed as “snapshots in time” as the cell cycles, and much more information can be obtained than with conventional techniques.”) We have also added a paragraph describing drawbacks of *ex situ* experiments in the Representative Results section.**

***in page 12, line 421-422: The authors could mention that this is the case when the element of interest is not present anywhere else along the battery (for example contacts or so).* A parenthetical comment has been added.**

***in page 12, line 423-424: It looks very weird to read that it takes 10-20min to change the energy of the monochromator in order to study another element's edge. Usually this is a matter of seconds.***

**This statement has been clarified in the text. While changing energies is very fast, associated tasks such as tuning, changing reference foils, etc. can take some time, so that there will be a gap in the data collection.**

***in page 12, line 425-426: The statement for the EXAFS is valid for many beamlines; however, when using state-of-the-art high-throuput setups, it is straightforward to get great EXAFS data very fast (few minutes).***

**The statement has been modified.**

***in page 13, line 440-442: The Authors quote that fluorescence mode probes only the surface and that penetration depth of x-rays is sub-micron. This is not valid for x-ray energies along the K-edges of 3d metals that it is mainly discussed in this paper. Fluorescence comes from several um to tens of um (depending on the electrodes composition).***

***in page 13, line 445-447: "Some fluorescence detectors also have much higher...". I guess the authors consider "fluorescence detectors" the single photon counting solid state detectors (like silicon drift detectors) and as transmission detectors the "ionization chambers" or "photodiodes". In that case there cannot be attempted any special comparison on the 'sensitivity' among these two type of detectors since their functionality is different in a fundamental way. The former detectors have energy resolving capabilities, and in fact are spectrometers (since they can measure an energy spectrum of the emitted radiation) and the latter 'detectors' are overall dose counters (so they integrate an overall current). The limitation of measuring dilute samples in a "transmission mode" is the negligible absorption within the sample and not the detector as a hardware component per se.***

***in page 13, line 448-456: the way this paragraph is written indicates some kind of confusion between the fluorescence-mode XAS and the transmission-mode of XAS. The authors need to mention explicitly for which mode they intend to refer to. The so-called "saturation effects" are present when fluorescence mode of XAS is attempted on highly concentrated non-thin samples (e.g. in the case of a thick sample, the 3d metal of interest needs to be less than ~0.1% per weight in order not to have any significant influence from self-absorption -aka saturation- effects within the recorded XAS spectrum). On the other hand, the one absorption length rule is relevant for the transmission mode of XAS. In the transmission mode there are not "saturation" effects like in fluorescence mode; however the experimentalist needs to keep the sample in such thickness that would allow the ion-chamber/photodiode to have enough transmitted signal when the incident beam will get over the absorption edge (sample not to be too thick) but at the same time to have enough contrast (the sample not to be too dilute).***

**The discussion on fluorescence mode has been removed, based on the comments above. A lengthy explanation of fluorescence vs. transmission modes is beyond the scope of this paper, but we have now summarized why these experiments are usually done in transmission, as indicated by this referee. We have also modified the discussion on sample preparation/thickness using information obtained at** [**http://xafstraining.ps.bnl.gov**](http://xafstraining.ps.bnl.gov)**, which is now referenced in the text.**

***Additional Comments to Authors:***

***The authors are citing many of their works (if i counted correctly, the 12 out of the 18 references are co-authored by some of the authors of the present paper). On the one hand this shows that they have done some significant amount of work toward studying battery materials, but i am sure we would all agree that it is favorable to provide a broader range of citations, when possible.***

**We have added the references included in this referee’s report (although we note that one that was suggested was co-authored by one of the authors of this manuscript). The point of this paper is, of course, to describe the synchrotron radiation experiments we are doing on battery materials, thus, citing our own work is inevitable.**

**The comments of this referee are comprehensive and insightful, and have helped us improve the paper. We appreciate the time s/he took in reviewing this paper.**

***Reviewer #3:***

***Manuscript Summary:***

***XAS and XRD can provide very useful information for a better correlation and understanding of material functionality and its physical and chemical properties. In particular, the in situ technique is of high interest, because it ensures that one can observe the real behavior of the material in operation. The manuscript describes the battery cell assembly for specific materials and gives a general idea how one can perform in situ and ex situ characterization by XRD and XAS based on synchrotron radiation. A detailed protocol how a beamtime at the SSRL synchrotron facility should be prepared is provided. The techniques of XRD and XAS are well described. In particular, the details about calibration and data evaluation should be helpful for new users. The strategies how to solve the main challenges of an in situ characterization based x-ray analytical techniques is quite general, somehow unspecific and of limited use for new users.***

**The manuscript is limited in scope due to length considerations. However, large parts of the protocol will be filmed and this should provide more information on the *in situ* techniques for the interested reader/viewer of the finished paper.**

***Major Concerns:***

***It is not clear for me how is addressed with this paper. Maybe scientists which are developing novel materials for Li ion batteries? On the one hand the authors provide a lot of details about the assembly of specific battery cells. These details are usually known by the material scientists. On the other hand important details about the in situ instrumentation are missing. One of the most important challenges is to design the in situ cell with x-ray transparent windows. Here, more details would be very helpful for the users. For example, what is a good thickness of the polyester foil for the x-ray windows, how thick the current collector foils can be etc. The thickness of the complete cell limits strongly the elements (e.g. S and Ti) which can be accessed by XAS. It would be helpful for users to get some experienced data about material thicknesses and limitations.***

***In many cases the authors propose to perform ex situ experiments including the advice to wash the cathode and anode material. In general the proposal is right in view of learning as much as possible before starting the significantly more sophisticated in situ experiments. But the authors do not explain the drawbacks of ex situ experiments. In particular, there are many effects, such as self discharge and chemical reactions with ambient air, humidity and the washing solutions. These effects could cause strong changes in the material between the electrical characterization and the ex situ XRD and XAS experiments.***

**The paper/film is intended for those who wish to learn the experimental techniques involved in performing *in situ* synchrotron radiation experiments on batteries. It may include both beamline scientists new to the world of batteries, who would like to apply their expertise, and to materials scientists working in the field of batteries new to synchrotron radiation techniques. Thus, brief descriptions of both the materials science and the synchrotron radiation technique aspects are included in the text. The purpose of the journal is to record in detail the procedures involved in certain types of experiments. A unique feature of this journal is the filming of the experimental procedures, which allows direct observation by the viewer.**

**Two very detailed tables of materials and equipment have been included with the manuscript. For example, the table of materials includes suggested thicknesses for pouches and Kapton films used to cover samples or contain the coin cells, as well as for the current collectors. It also includes suggested vendors and catalog numbers. The referee may have missed these during the review of the manuscript (or perhaps did not receive them). The tables should be very helpful for those who want to replicate the experiments for their own research.**

**A few sentences have been added to the manuscript summarizing the drawbacks of *ex situ* experiments and emphasizing the benefits of *in situ* work, as suggested by this reviewer and reviewer #2.**

**Minor Concerns:**

***For the background of both techniques XRD and XAS some additional hand books should be cited.***

***In the paragraph at line 439, the authors state the XAS in fluorescence mode is more surface sensitive than in transmission mode. This is not true, because the energy of the exciting x-ray beam is usually above the absorption edge and the energy of the emitted fluorescence x-rays is below. Hence, the absorption of the emitted x-ray is less attenuated than the exciting beam. Both XAS in fluorescence and transmission mode suffer from saturations effects if the sample thickness is too high. In the extreme case of an unlimited thick sample one can still measure XAS spectra in fluorescence mode, with strong saturation, but not in transmission mode. I think, the reason to perform the XAS measurements in transmission mode is that the in situ cell can be also used for XRD and maybe the design of the cell is easier.***

**We have added an on-line reference (**[**http://xafstraining.ps.bnl.gov**](http://xafstraining.ps.bnl.gov)**), removed the discussion of fluorescence, and clarified the sample thickness issue in the revised manuscript.**

***Additional Comments to Authors:***

***I really appreciate you effort to introduce and advertise to analytical possibilities available at synchrotron facilities. Most of the material research seems still very empirical to me. A reliable material characterization would be indispensable to achieve a more systematic progress. In particular, the in situ capabilities at the synchrotron facilities are very promising.***

***An Ex situ characterization of the material is usually questionable, because of the potential impact of handling under ambient conditions and washing for example. This can change the materials properties and makes a reliable correlation of material properties and functionality difficult.***

***Unfortunately, I have the impression that your paper can be hardly understand by scientists from material research. For potential users additional information would be helpful. The part about the different material combinations for battery cells can be shortened. A deeper discussion about ex situ vs. in situ measurements should be included. In addition, further details about the practical challenges for the in situ instrumentation and how one can solve them should be provided.***

**We have now included a paragraph outlining the drawbacks of *ex situ* experiments more explicitly, and emphasizing the advantages of *in situ* work. The description of battery materials (one paragraph in the Introduction) is necessary to provide the background and the rationale for doing synchrotron radiation experiments. This leads up to the Representative Results and Discussion section, in which specific examples from our previous work are used to illustrate the outcomes of the experiments. This format is required by the journal. The filming of the procedures will provide additional detail and is the main focus, with the written manuscript provided mainly as an aid to the viewer.**

**We thank this reviewer for helpful comments, particularly concerning fluorescence vs. transmission modes.**

***Editorial Comment: We understand that your protocol is focused on a specific set of experiments in order to fit the JoVE guidelines for video preparation and overall journal scope, and as such cannot encompass every aspect of this class of experiments in detail. However, please consider this reviewers comments and revise the protocol as you see fit to make it clearer and more useful to your targeted audience.***

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