Response to Technical Reviewers' Comments

R035-A

Preparation of Graphene-Modified LiFePO4 Cathode for Li-Ion Battery

University of North Dakota

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First, we would like to thank all three reviewers for their efforts. We are pleased to see that they recognize the merits of our project. Overall we feel it is fair to state that they agree that the objectives of the proposed work match the goals of NDIC/REC very well, and this is a strong proposal that has demonstrated the clearly defined market needs, well thought out R&D plan, and a thorough business plan for product scale-up. There is also agreement that the investigators have the adequate background, project management experience, resources, facility and equipment for success. We are thankful that Reviewer 1A completely overturned his opinion on the achievability (2) and methodology (3) of the revised proposal, resulting in a favorable overall comment. We have taken a look at the few identified weaknesses, and our responses are recorded herein.

2. With the approach suggested and time and budget available, the objectives are: 1 – not achievable; 2 – possibly achievable; 3 – likely achievable; 4 – most likely achievable; or 5 – certainly achievable.

Reviewer 1A (Rating: 3)

There revised preparation procedure is much more achievable than the previous proposal. The unknown is whether the proposer will obtain the intended small particle size, which will not be known until they try it. It is unlikely to achieve their claim that their procedure of drying/high temperature treatment is superior to spray drying to produce small particles. This comparison is well known in the field for many other materials. Since it is not known yet whether small particle size is critically important, they may still be able to obtain materials that meet their electrochemical performance target.

Our response: the reviewer is catching a very important point about the small particle size of the LFP/G. The small particle size is important to the battery performance, which is why many efforts have been conducted to reduce particle size of LFP to improve the battery performance. The reason we claim our procedure is superior to spray drying is because its simplicity, and thus its cost efficiency, not necessarily meaning its ability to produce smaller particles. Clean Republic's partner cell manufacturer has sufficient direct data showing that spray drying procedure tends to produce too large secondary particle size, which causes problems to the cathode preparation. As a matter fact, this drying step did not directly determine the particle size of the final product, since almost all the LFP cathode materials out of furnace must go through a standardized step -- regrinding prior to prepare the cathode composite. That re-grinding step is the control step for the particle size of LFP synthesized via solid phase reaction like ours and the conventional CTR method. We have purchased a Jet Mill (see appendix D) for that purpose. Our preliminary data are showing that the particle size by that equipment did meet our need for our battery performance target.

3. The quality of the methodology displayed in the proposal is: 1 – well below average; 2 – below average; 3 – average; 4 – above average; or 5 – well above average.

Reviewer 1A (Rating: 3)

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The proposed methodology is not innovative, but is achievable and on solid ground.

Our response: It is true there are many publication and patents on preparation and use of graphene/LFP in the literature, but we think "these existing research on the preparation of LFP/G normally require the synthesis of graphene in advance, which severely inhibits its practical applications, as cost-effective production of graphene at large scale is still a big challenge." The few in-situ synthetic technologies for LFP/G either need advanced equipment and expensive starting materials or complicated catalytic system and strict reaction conditions, and thus none of them are possible for mass production. On the contrary, our proposed technology is based on a proven synthetic procedure (carbothermal reduction) for LFP. It requires no special equipment, catalytic system, expensive starting materials and strict reaction conditions. That is why we can significantly reduce the cost for LFP/G and can easily upscale to mass production. In short, the concept of LFP/G is not innovative, but our in-situ technology to prepare LFP/G is certainly innovative and highly potential for mass production. Also, the achievability of this project is perhaps more important than being highly innovative as it is Clean Republic's goal to quickly adapt and implement this process if it proves successful.

Reviewer 3A (Rating: 3)

In situ synthesis of the graphene sheets in $LiFePO_4$ could be considered as a more effective approach compared with graphene coating on $LiFePO_4$, which requires the synthesis of graphene in advance and additional post-coating process. However, the proposed approach for high-purity and metal-free humic acid extraction from the leonardite is not proven. Implementation of an efficient process for humic acid extraction from the leonardite will be the most critical success factor of the proposed project.

Our response:

As the reviewer points out, optimization of the humic acid extraction process will be the most critical success factor for the proposed project. We list it as the first task of our R&D plan and a major challenge for the entire project (See the Confidential Information). Extraction of humic acid from leonardite (or Coal) is not a new concept, many procedures are in use (see reference 15, 16 and 17), as we have stated in the methodology section. However, humic acid extracted by those conventional approaches, such as alkali extraction, always contains a small amount of ash, in particular metal impurities that is not a problem for its common application as a fertilizer or soil supplement, but can cause a deadly problem to a Li-ion battery —failure of the battery. That is why there is no high purity of humic acid on the market: most vendors only supply up to 80% humic acids.

Fortunately, there are successful examples in the literature in which high purity and metal-free humic acid has been extracted from coal (Reference 32: Vermeer, A et al, *Langmuir* **1998**, 14 (10), 2810-2819). Our method is based on such a successful example but with significant modification. The main reason we won't simply copy their procedure to our project is their procedure is 1) too time-consuming (few weeks per batch) and 2) uses raw humic acid instead of much cheaper coal or similar as the feedstock. We will combine their concept with traditional alkali-extraction approaches to optimize our own extraction procedure. The key strategies are: 1) alkali-extraction and fractionation to obtain raw humic acid, 2) further purification by lixiviating agents, and 3) ultimate purification by dialysis and ion-exchange resin chromatography.

In the "**Techniques to Be Used, Their Availability and Capability** "section, we have provided an update about the current state of our extraction procedure. Only by using a lixiviating agent (step 2) without an optimized procedure, we are able to reduce the iron (the major unwanted impurity) content to 0.2% (vs

2.55% in raw leonardite, and 0.75% after alkali-extraction). Therefore, we strongly believe an optimized extraction procedure can achieve our goal to produce 99% and metal-free humic acid from ND leonardite.

From another angle of view, the 0.2% iron is equivalent to 0.02% in LFP (assuming the feeding amount of humic acid is maximum 10%), this small amount does not have substantial impact on the purity of LFP, as shown in Figure 1.

4. The scientific and/or technical contribution of the proposed work to specifically address North Dakota Industrial Commission/Renewable Energy Council goals will likely be: 1 – extremely small; 2 – small; 3 – significant; 4 – very significant; or 5 – extremely significant.

Reviewer 1A (Rating: 2.5)
There is a reasonable chance that this technology will generate material suitable for internal consumption in Clean Republic, so that Clean Republic does not have to pay market price for the cathode material. Whether the product can successfully compete in open market is highly questionable. The proposer has not put forward a convincing technical or economic case for a broad market appeal.

Our response: As the reviewer pointed out in Q3, the proposed technology is achievable and on solid ground. Based on our cost/profile structure analysis, we do believe our product can successfully compete with similar LFP cathode materials product in open market, provided the technical performance meet our goals. Of course, it is always risky to turn a lab-proven technology into an industry success, which is exactly why we are taking a low risk strategy to start with internal consumption in Clean Republic.

We do have a different opinion on "a convincing technical or economic case for a broad market appeal". Although Li-ion battery technology is increasingly improved, no single product can perfectly meet all the market needs. Therefore, battery manufactures would customize products for different applications rather than put forward a convincing "all-in-one" technology for a broad market appeal. This is why even the oldest technology $LiCoO_2$ (LCO) is still having a quite large market share. As a relatively matured technology, LFP is still one of the main streaming cathode materials for Li-ion battery. Its market potential is still quickly increasing (see our market analysis), especially in energy storage. Therefore, a high performance and low cost LFP cathode material to meet target market needs is still highly desired.

5. The principal investigator's awareness of current research activity and published literature as evidenced by literature referenced and its interpretation and by the reference to unpublished research related to the proposal is: 1 – very limited; 2 – limited; 3 – adequate; 4 – better than average; or 5 – exceptional.

Reviewer 2A (Rating: 2)
There is little discussion of the broader research activity in this general area of lithium ion battery cathode material, especially with respect to the competitive landscape of related technologies. The ones mentioned are those on the market, not those under development.

Our Response: There is a lot of literature in the general area of Lithium ion battery cathode material. Even the number of literatures on a much narrower topic--LFP cathode materials are already overwhelming. Limited to the page length of the proposal, we could only focus on the research activities relevant to ours. Our awareness of such relevant activities has been demonstrated in the section of "**Why the Project is Needed.**" More important, our proposed project is not to develop a radically new cathode material but to significantly improve the performance and reduce the cost of an existing cathode material, and to make a profit by implementing it for mass production. Those products/technologies under development are not in our competitive landscape yet, and often take 5 years or more to be commercially ready.

6. The background of the investigator(s) as related to the proposed work is: 1 – very limited; 2 – limited; 3 – adequate; 4 – better than average; or 5 – exceptional.

Reviewer 1A (Rating: 3)

The proposer does not have experience in electrode material development or introducing new manufacturing capability in battery. Their general technical background is good and should be helpful for this research and development.

Reviewer 2A (Rating: 4)

This is a strong research team with good qualifications, and a local partner in Clean Republic with real world business knowledge. One gap is potentially in large-scale manufacturing – Clean Republic is a downstream customer of cell manufacturers and as such may have limited ability to engage upstream manufacturers around the optimization of the technology. This gap wasn't really addressed in the revised proposal, but I'm not trying to be pessimistic on this score either, just calling it out as an area that will require special attention.

Our response: Beyond our general technical background mentioned in the proposal (page 10), our team has been conducting a LFP cathode material development project funded by Clean Republic and ND research venture grant for four years. The Dakota Lithium $LiFePO_4$ battery, manufactured by Clean Republic, is one of their primary products. The experience can be directly applied to this proposed project. In addition, our technical consultant Dr. Mo is running two $FePO_4$ manufacturing factories with the total annual production capacity more than 10, 000 tons. His experience and advises will be useful resource for our project. Fundamentally, Dr. Michael Mann, director of this project has over three decades' experience in a wide variety of energy applications. His experience in fuel cell development over the past 15 years was focused primarily on electrode assembly which is directly parallel to the current battery development activities.

10. The proposed budget "value"[1] relative to the outlined work and the financial commitment from other sources[2] is of: 1 – very low value; 2 – low value; 3 – average value; 4 – high value; or 5 – very high value. (See below)

Reviewer 1A (Rating: 3)

If securing another external funding source is successful, this is a good leverage of ND fund. Otherwise, it is unclear what is the leverage.

Our response: Excitingly, because of the significant technique breakthrough and tremendous business potential, our ongoing project fund by Research ND venture grant has attracted strong interest of external investment. Clean Republic has secured a $1.5 million USD investment from Aifloo AB, a Sweden private investment firm lead by Christer Staaf, on the LFP powder project and the relevant Dakota Lithium Battery production.

Timing of Future Grant Funding

We would also like to comment on the importance of timing of this grant. As you are aware, we are in the final stages of our Research ND grant. The results from this grant are successfully demonstrating that we can indeed produce consistent, high quality lithium phosphate cathode material, the original goal of the proposed effort. The final aspects of the project that are in progress include high purity (>99%) LFP powder with well-controlled particle size distribution (D_{50}<2 um and D_{90} <10um), better than proposed battery performance (130 mAh/g vs 120 mAh/g proposed), the ability to reproduce the same high quality of LFP at one kilogram-scale as at 20 gram-scale, only one-step away to the proposed final goal of pilot scale (10-kilogram level), and establishment of our own capacity to assembly and test coin-type cells beyond the proposed scope of work. These results in themselves will help Clean Republic differentiate their product from their competitors. The work proposed to the Renewable Energy Council will make another incremental improvement in their battery technology.

As a part of the Research ND project, we have assembled a strong working team, including several undergraduate and graduate students. We proposed to this funding round to ensure continuity between the two projects. Waiting for the completion of the Research ND project before applying for follow-on funding would result in a 6 to 9 month funding gap. Our current students will have moved on to other projects. Our equipment will need to be idled, and extra time will need to be spent to restart, recalibrate and retrain. Momentum is always lost when a project is shut down for a period of time.

Perhaps more importantly is the time to market concerns. The area of battery development is evolving quickly. The big winners will be those who are first to market. A six to nine month delay could compromise the potential market share of Clean Republic. Therefore, we feel it is important to start this new project directly upon the completion of our Research ND project, and not delay funding until the next funding round.