Contract No. R-035-044

"Preparation of Graphene-Modified $LiFePO_4$ Cathode for Li-Ion Battery"

Submitted by: University of North Dakota

Principal Investigator: Xiaodong Hou / Dr. Michael Mann

PARTICIPANTS

Sponsor	**Cost Share**	
Clean Republic	$457,873	
Subtotal Cash Cost Share		$457,873
North Dakota Industrial Commission	$238,366	
Total Project Cost		$696,239

Project Schedule – 2 years
Contract Date – 3/6/2018
Start Date – 3/1/2018
Completion Date – 3/31/2020

Project Deliverables:
Semi-Annual Report: August 31, 2018 ✓
Semi-Annual Report: March 31, 2019 ✓
Semi-Annual Report: August 31, 2019
Final Report: March 31, 2020

OBJECTIVE/STATEMENT OF WORK:

The objective of this project is to prepare graphene-modified lithium iron phosphate cathode materials (LFP/G) at pilot scale (10 tons/year.) The project will extract and purify humic acid from North Dakota sourced leonardite. The end goal is to produce an improved battery that will be utilized initially within Clean Republic on their E-bikes. The batteries are expected to have more power, a longer battery life, and perform better in low temperatures.

The 66% match ($457,873) comes from Clean Republic

If successful, this project will create high-performance low-cost cathode materials for Li-Ion batteries and associated preparation processes. The cathode production has the potential to generate revenue of $2.4 million/year and 12 full time employees by 2023. This project could provide market diversification for North Dakota leonardite while also creating new manufacturing opportunities in the state.

Two contingencies were approved by the Industrial Commission -- 1) Research ND project is successfully completed prior to releasing any Renewable Energy Program funding; 2) If the project is not having success with materials from Leonardite Products based in Williston, the applicant will try using leonardite from other North Dakota sources including American Colloid located in Bowman County and Falkirk Mine.

After the application was submitted, the applicant revised the budget to increase the match provided by Clean Republic from $247,873 to $457,873.

STATUS:

The contract has been executed.

August 2018

Five tasks have been defined to fulfill the above goals. In the past six months, the project is focused on the task 1 as planned in the time lines. The progress is outlined as follows:

1. The task 1 is completed and two humic acid extraction procedures were optimized and compared with the two key objectives of the highest yield and purity.
2. In the first approach—alkali extraction, a Taguchi orthogonal array design L9(34) with 4 factors at 3 levels and a total of 9 runs was implemented. An optimized procedure is determined with a balance between the purity and yield.
3. A solvent extraction procedure is also studied for comparison. A similar Taguchi orthogonal array design L9(34) with 4 factors at 3 levels and a total of 9 runs was implemented. An optimized procedure is determined with a balance between the purity and yield.
4. With all factors considered, the alkali extraction technique is superior to the solvent one and will be used for the rest of the project. The basic extraction technique is far superior in terms of percent yield, producing nearly 140% of the maximum amount of humic acid that can be obtained through solvent extraction. The solvent extraction does have a slight edge over the basic extraction method in terms of overall purity. However, the alkali extraction is again superior when it comes to reducing iron content, with a projected reduction to below 1%, while the solvent extraction method results in a final iron content of 1.24%.
5. To further reduce the iron content down to target value of 0.5% or less, a second purification step is used to treat the alkali extracted raw humic acid, now we can reduce the iron content down to only 0.2%. This primary result indicated that a simple alkali extraction plus a second purification treatment could produce the satisfactory humic acid for LFP/G preparation.

With the purified humic acid by Task 1 as a key feedstock, we just start the Task 2. This task and Task 3 will be focused on the optimization of the synthetical procedure of LFP/G.

March 2019

In the past six months, the project is focused on the task 2 and part of the task 3 as planned in the time lines. But we adjust the schedule slightly according to the project progress and facility availability. For example, we proceed some work in Task 4 and 5 ahead of time. The progress is outlined as follows:

- Task 2, optimization of LFP/G synthesis procedure is in the final stage, will be completed by March 30, 2019.
    - A series of LFP/G samples have been prepared. Coin cells prepared with these samples have exhibited increased high-rate performance, and specific capacity close to the target value.
    - Minitab statistical software was again utilized to design a series of experiments to optimize the LFP/G synthesis procedure. Experiments were set up as a Taguchi orthogonal array design L9(34), testing four factors at three levels each with a total of 9 runs.
- Task 3, characterization of LFP/G cathode has seen some results.
    - XRD spectra of the LFP/G sample shows expected >99% crystalline purity.
    - XRD spectra of LFP/G samples exhibited sharp peaks corresponding to highly graphitized carbon.
    - Under SEM, LFP/G samples had few carbon agglomerations, indicating the humic acid has formed thin, even coatings on the LFP particles.

- Task 4, Pilot scale production has proven to be scalable based on optimized extraction procedures at lab scale.
    - A few kilogram humic acid was prepared at pilot scale using equipment for an adjacent project.
    - Separating liquids and solids via filtering was the single-most time consuming step. We have developed a novel staged and pressure-driven filtering that can mitigate this problem and the technology could have broad application in other similar fields.
- Task 5, electrochemical performance testing is currently being conducted on cell prepared with our LFP/G cathode material.
    - Cells have exhibited good rate performance at high discharge rates, compared with commercial LFP/C.
    - The specific capacity of the cathode material is currently around 148 mAh/g. This is expected to increase to 150 or more upon the completion of Task 2.

Updated 7/10/2019