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Economically Viable "Green" Carbon Anodes for Lithium-Ion Batteries from Recycled Scrap Tires

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OAK RIDGE NATIONAL LABORATORY
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Chemical Sciences Division
Advanced Manufacturing Office

Economically Viable "Green" Carbon Anodes for Lithium-ion Batteries from Recycled Scrap Tires

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ACKNOWLEDGEMENTS

This CRADA NFE-16-06387 was conducted as a Technical Collaboration project between Oak Ridge National Laboratory (ORNL) and Lawrence Berkeley National Laboratory (LBNL) sponsored by the US Department of Energy Advanced Manufacturing Office. The goal of technical collaborations is to engage industry partners to participate in short-term, collaborative projects to assess applicability and of new energy efficient manufacturing technologies. Research sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, under contract DE-AC05-00OR22725 with UT-Battelle, LLC. Thanks are due to Gabriel Veith with LIPON coating.

1. Abstract

The technical objective of this technical collaboration small business voucher (SBV) proposal was to develop methods at Oak Ridge National Laboratory (ORNL) to reduce the surface area and impurity contents present in the recovered carbon from scrap tires. Recycled tires have been used to make low-cost carbon anodes for lithium-ion batteries (LIB) with a cost-reduction of over 11-12%. Graphite is being used as the anode in LIBs. Oak Ridge National Laboratory (ORNL) has successfully recovered carbon composites from recycled tires with a yield of over 50% and demonstrated the electrochemical performance in a coin lithium ion cell configuration as an active anode material better than commercial graphite anode batteries [1]. ORNL has tailored the morphology of carbon powders from shredded recycled tires using a sulfonation process followed by pyrolysis to produce a highly value-added product and demonstrated its feasibility in LIBs. ORNL developed the methods to reduce impurities and surface area and provided carbon to Lawrence Berkley National Laboratory (LBNL) for detailed characterizations including lithium-ion battery testing. This SBV pilot project will also provide R&D infrastructure to FWD:Energy, Inc. (FWD) to establish a pre-pilot process to scale-up the synthesis of carbon composites from recycled tires and illustrate a high value commodity for anodes in large format LIBs.

2. Statement of Objectives

This SBV project was started in March 2017, and completed in December 2017. The collaboration partner, FWD:Energy, is focused on bringing to market a set of leading edge technologies to manufacture critical materials for advanced energy storage:

- FWD's patent pending VersaWave™ unifies industrial microwave and vibratory conveyance into a single process for continuous, high throughput conversion of waste tires
- Licensed technology competitively awarded by ORNL upgrades converted tire carbon into a hard carbon substitute for graphite in LIB anodes.

The purpose of this contract is to define ORNL and LBNL's specific role in collaboration with FWD under the DOE Small Business Voucher Program. Materials researchers work closely with industry to develop and evaluate their tire derived carbon technologies; the staff selected for this project provides particularly relevant expertise in recovery of carbon, lithium ion battery research, and materials characterizations. By leveraging the capabilities of LBL and ORNL to create a scalable process for removal of impurities, FWD would be able to manufacture high performance anode carbon at a cost much lower than foreign-sourced anode graphite. The main goal of this research is to develop a method or process to reduce the impurities and surface area of carbon and possibly improve the first cycle efficiency of tire-derived carbon to > 85%.

3. Benefits to the Funding DOE Office's Mission

It is estimated that every year more than 1 billion end-of-life tires are generated worldwide, posing serious hazards to public health and the environment. Successful implementation of this technology would result in a significant reduction in carbon emissions (from about 6500 lbs./ton for virgin carbon black to about 3650 lbs./ton for recycled carbon composites; improving the net energy value from about 32 million British thermal units (MBU)/ton to about 44 MBU/ton) and result in a lower-cost higher performance LIB. It will also facilitate the development of a LIB technology to achieve the energy efficiency and competitive cost required to successfully implement into the electric car technology. FWD seeks the assistance of the DOE National Labs to scale up this impurity removal process to commercialize breakthrough material that would give competitive advantage to USA battery manufacturers. The project goals are consistent with the DOE

ARPA-E and EE&RE Plug-in Electric Vehicle (PEV) program goals of reduction in battery cost and licensing of Oak Ridge National Laboratory's technology to US manufacturers. Overall, the advancement of the lithium-ion battery anodes could lead to the adoption of battery technology by battery manufacturing companies, and lead to job growth and higher US global manufacturing competitiveness.

4. Technical Discussion of Work Performed by All Parties

FWD:Energy has developed a cost competitive thermal conversion technology that can produce tire-derived carbon for Li-ion batteries. The one limitation of the material is its poor first cycle irreversible capacity. It is believed that this is the result of a material with high surface area and high impurity content. During this year we intend to improve processing conditions to reduce both. ORNL and LBNL worked closely with FWD to accomplish this goal. ORNL possesses capabilities to tailor the microstructure of tire-derived carbon and to reduce both surface area and impurity contents through process optimization, coatings methods and lithium-ion battery testing. LBNL possesses capabilities to measure the impurity content by ICP or EDX, to measure the surface area by particle size analysis or BET surface area analysis, and to measure the reversible and irreversible capacity in half cells. LBNL also possess the capability to measure the rate of side reactions after the first cycle in half cells and full cells to measure its effect on cell capacity fade.

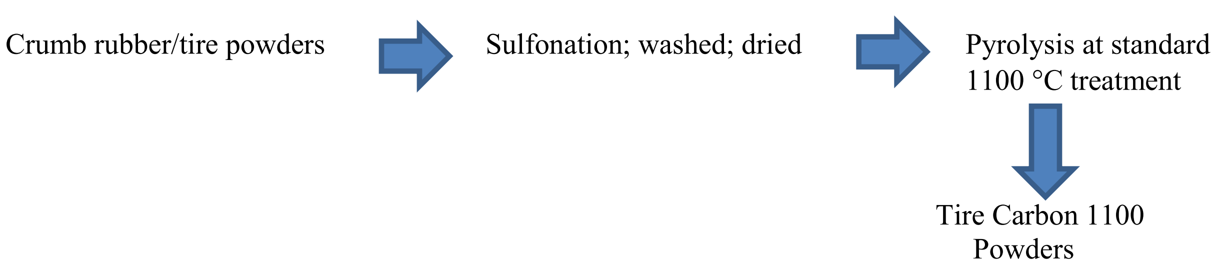
Tasks
The following proposed tasks were conducted by Oak Ridge National Laboratory to improve the properties of the recovered carbon from recycled tires.

<u>Task 1. Tailoring the microstructure of carbon</u>
ORNL optimized the acid treatment conditions of crumb tire pieces or tire powders and pyrolyzing temperatures and residence times. Detailed characterizations were carried out on the composite powders to determine if we meet the specification of particle size, geometry and capacity. Optimized carbon samples were sent to LBNL for further physical characterizations.

<u>Task 2. Carbon coating process</u>
For each change in processing conditions, a set of carbon materials prepared at ORNL and coated using toluene followed by post-annealing studies. The materials were characterized to see whether the surface area is reduced and any influence on the microstructure and porosity.

<u>Task 3 Half Cell Assembly and Testing</u>
Performed coin cell testing to benchmark the results using standard electrolytes and lithium as the counter electrode and performed detailed electrochemical characterizations.

<u>ORNL path towards achieving the FWD goal:</u>



(I) Tire carbon 1100 (with and without carbon coating (via annealing))

(II) Tire carbon 1100 in hydrochloric acid treatment (to dissolve impurities) (with and without carbon coating)

(III) Tire carbon 1100 in nitric acid treatment (to dissolve impurities) (with and without carbon coating)

(IV) Tire carbon 1100 – anneal in hydrogen atmosphere (Ar/H_2 4%) (to reduce oxygen content) (with and without carbon coating)

(V) Tire carbon 1100 with LIPON (high lithium ion conductor) coating (two conditions) (another way of coating to reduce the surface area and also improve lithium transfer)

(VI) Tire carbon 1100 with hydrofluoric acid treatment (to remove silica) (with and without carbon coating)

(VII) Tire carbon 1100 with hydrofluoric acid treatment (to remove silica) and coat it with polymer such as PVAc in methanol/water and anneal (similar to FWD energy procedure)

(VIII) Based on the data from various carbon produced, we identified conditions to bring the impurity levels as low as possible.

The following proposed tasks were conducted by Lawrence Berkeley National Laboratory on a repetitive basis with each carbon produced by ORNL aimed to improve the carbon. ORNL provided more than 20 different forms of carbon to LBNL for testing.

Task 4. Physical Characterization

Each material received were characterized for its physical attributes, most importantly, its BET surface area and its particle size distribution. SEM was also used to attain the material's overall shape and to assess whether the surface area measured by BET can be ascribed to its external size and shape or if there is a contribution from within the particles. The elemental composition of the impurities will be measured using ICP-OES and the distribution of impurities assessed using EDX.
Task 4.1 Performed BET and PSA of all materials received to assess surface area and particle size distribution, respectively.
Task 4.2 Performed SEM and EDX on all materials received to ascertain particle morphology and chemical distribution on the surface.
Task 4.3 Performed ICP-OES to measure impurity levels.

Task 5. Anode Fabrication and Cell Assembly

For each change in processing conditions, a set of materials were received from ORNL and manipulated into electrodes. The materials were tested in coin cells to determine their first cycle reversible and irreversible capacities, cycleability, and rate of side reaction at a given discharge rate.

Task 6. Electrochemical Characterization

Half-cells were constructed in coin cell hardware to measure the electrodes' reversible capacity, first-cycle irreversible capacity loss, and cycleability.

Task 6.1 Performed electrochemical characterization of each cell, including, cell cycling, HPPC testing, and cycling. Reported results to FWD: Energy and ORNL
Task 6.2 Developed a consistent list of metrics to identify the overall best material.
Task 6.3 Prepared graphs of the data and reported back to FWD: Energy and ORNL. The results are reported in Tables 1 and 2.

Table 1. The physical properties and electrochemical properties of carbon recovered from scrap tires.

	Physical Properties		Electrochemical Properties					
	BET surface area g/m^2	Carbon Content (%)		$Q_{re.}$ (mAh/g of active material) at the 5th cycle	$Q_{re.}$ (mAh/g of carbon) at the 5th cycle	V_{ave} 0.05 C/0.3 C	Specific energy at the 5th cycle (Wh/kg of electrodes)	**Specific Energy (prelithiation- No excess LCO)**
MCMB	2.7721	98.9	90.1	295.1	289.4	3.63/3.62	285.5	317.2
Carbotron	1.6740	99.3	83.7	284.6	286.6	3.33/3.39	238.0	290.4
Optimized TC-1100 (Goal)	2.69	100	83	430	430	3.3	**277.5**	325.7
TC-1100-C9	31.1207	88.6	57.3	371.9	419.8	3.27/3.29	181.5	310.3
TC-1100-#2	56.7377	87.7	54.1	317.7	362.3	3.26/3.28	162.2	294.9
TC-1100-HCl-C9	24.0782	86.2	56.6	296.0	343.4	3.27/3.27	161.4	289.0
TC-1100-HF-C	More sample	90.1	63.0	288.6	320.3	3.24/3.26	169.2	283.9
TC-1100-LiPON1	32.2346	82.0	55.1	279.5	340.8	3.25/3.26	150.6	281.6
TC-1100-NAT-C9	75.0976	86.8	54.0	277.4	319.6	3.25/3.25	149.3	280.9
TC-1100-NAT-H2	170.813	84.3	50.6	274.3	325.4	3.23/3.26	140.3	278.1
TC-1100-HF-NH4OH-C	28.8418	91.0	58.7	273.9	301	3.23/3.26	154.3	277.9
TC-1100-HCl	35.7986	84.2	52.6	268.5	318.9	3.24/3.25	142.4	276.8
TC-1100-#1	74.8378	81.7	40.6	310.8	380.4	3.07/3.14	103.5	275.7
TC-1100-LiPON2	More sample	83.0	53.3	263.9	318.0	3.24/3.24	141.9	275.1
TC-1100-HF-NH4OH	16.8975	91.4	56.1	270.8	296.3	3.20/3.22	145.4	274.3
TC-1100-NAT	54.0119	83.4	54.2	260.1	311.9	3.24/3.25	144.2	273.0
TC-1100-H2	119.51	85.9	51.9	247.6	288.2	3.23/3.25	132.4	267.9
FWD	11.6147	91.7	62.9	242.7	264.7	3.26/3.28	168.6	268.4
TC-1100-HF-III	9.3213	92.4	53.5	240.5	260.3	3.23/3.26	137.6	265.0
TC-1100-HF-III-C	42.0529	96.2	41.1	221.2	230.0	3.18/3.24	97.5	252.4
TC-1100-HF	3.4001	89.6	48.6	202.1	226.1	3.18/3.22	111.5	243.4
TC-1400	234.0749	90.2	45.8	173.6	192.5	3.34/3.39	106.8	238.7
TC-1100-KOH	More sample	86.3	More sample	More sample	More sample	More sample	More sample	More sample
TC-1100-KOH-C	More sample	90.1	More sample	More sample	More sample	More sample	More sample	More sample

Table 2. 1st cycle specific capacity and Coulombic efficiency of carbon recovered from scrap tires.

	$Q_{disch.}$ (mAh/g of active material)	$Q_{re.}$ (mAh/g of active material)	C.E. (%)
FWD	386.8	243.5	62.9
TC-1100-#1	949.3	385.0	40.6
TC-1100-#2	573.3	309.9	54.1
TC-1100-C9	630.3	360.9	57.3
TC-1100-HCl	528.4	277.8	52.6
TC-1100-HCl-C9	533.7	302.3	56.6
TC-1100-NAT	501.6	271.9	54.2
TC-1100-NAT-C9	515.2	278.3	54.0
TC-1100-H2	515.2	267.4	51.9
TC-1100-NAT-H2	544.6	275.8	50.6
TC-1100-HF	461.0	224.3	48.6
TC-1100-HF-C	497.9	313.6	63.0
TC-1100-HF-III	471.4	252.2	53.5
TC-1100-HF-III-C	595.9	245.3	41.1
TC-1100-HF-NH4OH	526.6	295.8	56.1
TC-1100-HF-NH4OH-C	508.0	298.1	58.7
TC-1100-LiPON1	531.0	293.1	55.1
TC-1100-LiPON2	520.9	277.8	53.3
TC-1400	396.2	181.3	45.8
Carbotron	351.1	294.1	83.7
MCMB	318.23	286.63	90.1

The following summary was observed based on the data developed on various carbon.

1. FWD and ORNL powders showed the rough surface and a lot of nano-particles.
2. FWD and ORNL samples showed high impurity contents (12~18%) and large BET surface area.
3. The carbon coating process successfully reduced the BET surface area and increased C content, which result a slight enhancement of initial Coulombic efficiency.
4. Although TC-1100-C9 showed the highest specific capacity, obtainable specific energy of the cell coupled with LCO electrode is not as good as those of MCMB and Carbotron, which is mainly due to the low initial C.E. (57.3 %, excess amount of LCO is required) and high impurity level (11.4 % attribute to the dead weight).
5. It was demonstrated that neither the impurity content nor the BET surface area has correlation with the initial C.E.
6. The surface area was reduce to 3.4 m^2/g with HF treated carbon powders.
7. The KOH and the HF treatments reduced Si and O content. The highest carbon content of 96.2 was observed for HF treated carbon powders. The highest first cycle Coulombic efficiency of 63% was observed.

8. To conclude, methods were developed the reduce the surface area and impurities with carbon recovered from scrap tires.

5. Subject Inventions (As defined in the CRADA)

The method developed for the carbon purification didn't improve the first cycle Coulombic efficiency. Further work is necessary to improve the first cycle efficiency before it can be patented.

6. Commercialization Possibilities

Carbon recovered from scrap tires offer a better option for making low cost graphite anodes for lithium-ion batteries. Here we demonstrated a novel approach to reduce the impurities and surface area of carbon. Further improvements are necessary with carbon to improve the first cycle efficiency.

7. Plans for Future Collaboration

Tire-derived carbon offers significant advantages such as cost effectiveness of producing anodes for lithium ion batteries. FWD will work with ORNL and LBNL in the near future towards optimizing tire-derived carbons for this application.

8. Conclusions

In this work, we report the feasibility of reducing the surface area and impurities present in the tire-derived carbon. Preliminary results are promising. Further process optimization is necessary to improve the first cycle Coulombic efficiency.

9. References

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