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For
CRADA Number NFE-10-02757

Optimization and Domestic Sourcing of Lithium Ion Battery Anode Materials

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Optimization and Domestic Sourcing of Lithium Ion Battery Anode Materials

1. Abstract

Cost is a major barrier limiting the introduction of lithium ion batteries into the plug-in hybrid electric vehicle (PHEV) and electric vehicle (EV) markets. Materials comprise 70% of the battery cost, and nearly all of the key materials suppliers are based in Asia. This project addressed an opportunity to leverage low-cost available anode materials through applying new treatments to improve anode materials to match high performance cathodes. In this project, A123 Systems teamed with the ORNL Carbon Materials Group to correlate graphitic anode powder attributes to raw material characteristics and process conditions. The results guided decisions on anode selection and the establishment of domestic supply base for anode materials. The establishment of this supply base is vital to reduce lithium battery costs and support the success of US manufacturers of lithium batteries for transportation and grid storage markets.

The purpose of this Cooperative Research and Development Agreement (CRADA) between ORNL and A123Systems, Inc. was to develop a low-temperature heat treatment process for natural graphite based anode materials for high-capacity and long-cycle-life lithium ion batteries. Three major problems currently plague state-of-the-art lithium ion battery anode materials. The first is the cost of the artificial graphite, which is heat-treated well in excess of 2000°C. Because of this high-temperature heat treatment, the anode active material significantly contributes to the cost of a lithium ion battery. The second problem is the limited specific capacity of state-of-the-art anodes based on artificial graphites, which is only about 200-350 mAh/g. This value needs to be increased to achieve high energy density when used with the low cell-voltage nanoparticle $LiFePO_4$ cathode. Thirdly, the rate capability under cycling conditions of natural graphite based materials must be improved to match that of the nanoparticle $LiFePO_4$.

Natural graphite materials contain inherent crystallinity and lithium intercalation activity. They hold particular appeal, as they offer huge potential for industrial energy savings with the energy costs essentially subsidized by geological processes. Natural graphites have been heat-treated to a substantially lower temperature (as low as 1000-1500°C) and used as anode active materials to address the problems described above. Finally, corresponding graphitization and post-treatment processes were developed that are amenable to scaling to automotive quantities.

2. Statement of Objectives

The goals of this project were threefold. An ideal natural graphite anode material was identified from the investigated material set. A low-temperature heat treatment process was then tailored for the

selected natural graphite material. These first two goals were met in parallel. The third goal was to optimize the heat treatment process and post-treatment for scale up.

The desired result was identification of a natural graphite material that only needs to be heat-treated to <2000°C and that demonstrates improved specific capacity and rate capability. The performance of the final materials was demonstrated in full-active-area pouch cells, and the heat treatment and post-treatment processes were vetted for scalability. To achieve this result, a great deal of heat-treatment trials and associated material characterization of the raw and post-treated materials was required.

Thorough chemical, crystallinity, and microstructural characterization of a raw materials set of natural graphites and baseline artificial graphites was completed, and this information was fed into developing a heat treatment process. Both surface and bulk features were studied. The main heat-treatment parameters that were optimized were ramp times, hold temperatures, hold times, maximum temperature, ramp-down conditions, and furnace atmosphere. Post treatments of the graphite surface were also investigated. The heat-treated and post-treated anode active materials were subsequently characterized for material and chemical changes, which were further correlated with electrochemical test data. Using the characterization and electrochemical data a final heat treatment procedure was refined and implemented.

3. Benefits to the Funding DOE Office's Mission

The primary DOE sponsor of this project was the Office of Energy Efficiency and Renewable Energy (EERE) Advanced Manufacturing Office (AMO) – formerly the Industrial Technologies Program (ITP). The project was co-sponsored by the EERE Vehicle Technologies Program (VTP). This project represents one of ORNL's key energy storage objectives, which is to partner with battery manufacturers to investigate, improve, and scale process methodology for manufacturing of high performance lithium secondary batteries in significant quantities. In addition, characterization of key materials and components will complement the advanced processing research and manufacturing science. These aspects are well aligned with AMO's mission, which includes energy efficient scaling of new technologies and cost reduction of manufacturing steps critical to the nation's energy infrastructure.

Results of a Government Performance and Results Act (GPRA11) analysis for this project showed that the potential energy savings associated with the new anode raw material heat treatment protocol was substantial. The energy savings potential of this technology was calculated on the following basis. In 2013 the Livonia, Michigan plant will produce 24,000 plug-in hybrid electric (PHEV) battery packs with 16 kWh of energy storage and 320,000 hybrid electric vehicle (HEV) packs with 1.6 kWh of energy storage for a total annual production capacity of 896 MWh (one unit-year). For simplicity, only equivalent USABC-sized PHEVs (11.6 kWh per battery pack) were used to estimate vehicles manufactured per unit-year. In this case, one unit-year equals 77,240 equivalent PHEVs. An amount of 0.90 kg of anode graphite is used per kWh of energy storage, so a total of 806,400 kg/year is required. At a cost of $20/kg of anode graphite and an assumption that 50% of the production cost is heat-treatment electricity, $8.06M is spent on anode graphitization alone. Energy benefits resulting from this project will occur through the substitution of high-temperature synthetic graphite with low-temperature

natural graphite. This will save as much as 75% in heat-treatment electricity (which is $6.05M/year). Since the high-temperature graphitization is done during off-peak hours, an electricity cost of $0.075/kWh may be assumed, which translates into a savings of 81 GWh/year (2.8×10^{11} Btu/year or 0.00028 quad/year). Corresponding unit inputs are 0.108 billion kWh for the current technology and 0.0269 billion kWh for the new technology. The cumulative production energy savings including continued scaling and constructing of new plants through 2020 based on implementation of this anode processing technology is estimated at 4.8 trillion Btu.

The analysis may also be extended to include the equivalent domestic petroleum distillate savings in 2020. An average gasoline savings of 20 miles/gallon is assumed for a HEV/PHEV over an internal combustion (IC) engine. For an average annual driving distance per vehicle of 10,000 miles, 500 gallons/vehicle of gasoline would be saved annually. Estimates for the total 2020 xEV market were taken from the 2008 Rocky Mountain Institute study, which predicts 4.1 million HEVs (assumed average of 1.6 kWh per battery pack), 5.6 million PHEVs (11.6 kWh per battery pack from USABC data), and 0.45 million EVs (40 kWh per battery pack from USABC data). These predictions correspond to a total storage capacity of 89.5 GWh and 7.72 million equivalent PHEVs. From the GPRA11 analysis for this project, a predicted equivalent PHEV market share of 4.0% was estimated for 2020, which corresponds to 3.5 million barrels of petroleum distillate saved.

4. Budget

This project was funded by AMO at a level of $449k over the 30-month duration, and it also included $208k from VTP. The DOE project total of $657k was cost shared by A123 Systems at a level of $840k (56% in kind). The spend plan by project year (PY) for the CRADA is shown in the table below:

Table 1. Spend plan for CRADA NFE-10-02757 between A123 Systems, Inc. and ORNL.

Parties	PY 1	PY 2	PY 3	Total
DOE's Contribution via ORNL	$269,115	$258,591	$129,294	$657,000
A123 Systems In-Kind	$280,730	$372,848	$186,422	$840,000
Total	**$549,845**	**$631,439**	**$315,716**	**$1,497,000**

5. Technical Discussion of Work Performed by All Parties

The following discussion on the technical results is organized into sections based on the different objectives set forth in the original CRADA statement of work.

5.1. Microstructural and Chemical Characterization of Anode Materials

Three baseline graphite samples were received in April 2010 for characterization and conducting the initial heat-treatment matrix. BET surface area, thermogravemetric analysis (TGA), temperature programmed desorption mass spectroscopy (TPD-MS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were completed on each of the untreated samples. All preparations for the heat-treatment runs were made including furnace selection, temperature set points, furnace cooling protocols, and crucible construction. Figure 1 shows XRD data of the three different baseline graphite

materials with no heat treatment. It is seen that the natural graphite (NG-15) and artificial graphite (ARG) have strong graphitic signatures, and the shapes of the peaks confirm that the grain sizes of NG-15 are larger than those of ARG. The mesoporous carbon microbead (MCMB) sample was found to be highly amorphous and is likely not even fully carbonized (see Fig. 1). It was also found that NG-15 contained a 2:1 ratio of hexagonal to rhombohedral crystalline structure. Surface O and N content was investigated with XPS and the results are shown in Figure 2. It was determined that NG-15 graphite had 2× the amount of surface O as ARG and 3.5× the amount as MCMB. No surface N was measured for either NG-15 or MCMB.

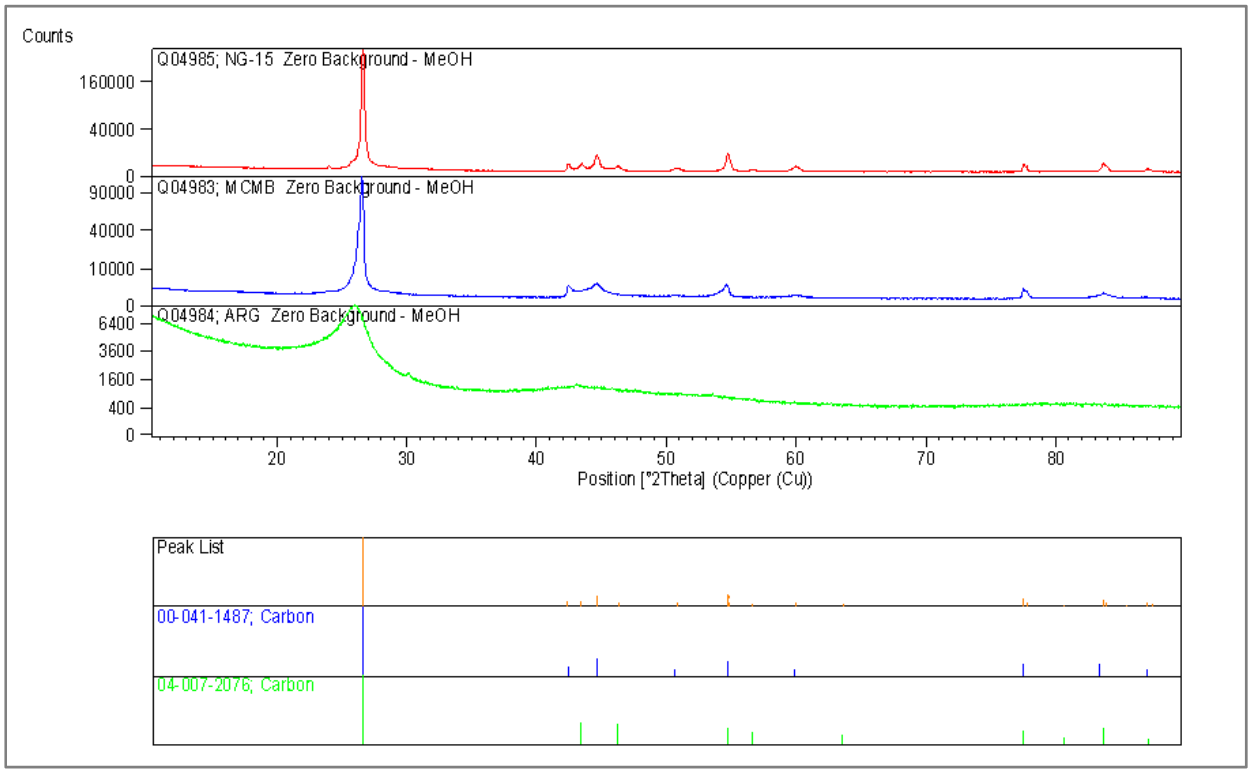

Figure 1. XRD results of three different untreated graphite samples showing markedly different structure of artificial graphite (ARG).

Three sets of materials underwent heat-treatment processing at ORNL, which consisted of artificial graphite, natural graphite, and carbon-coated natural graphite. The first round of heat treatments was completed in July and August 2010. Based on materials characterization (XRD, XPS, SEM, TEM, TPD-MS and Raman spectroscopy) and coin cell performance data taken at A123 Systems, a focus was placed on 950°C, 1050°C, and 2000°C. These temperatures represent a substantial reduction of the commonly used graphitization temperatures of 2500-3000°C.

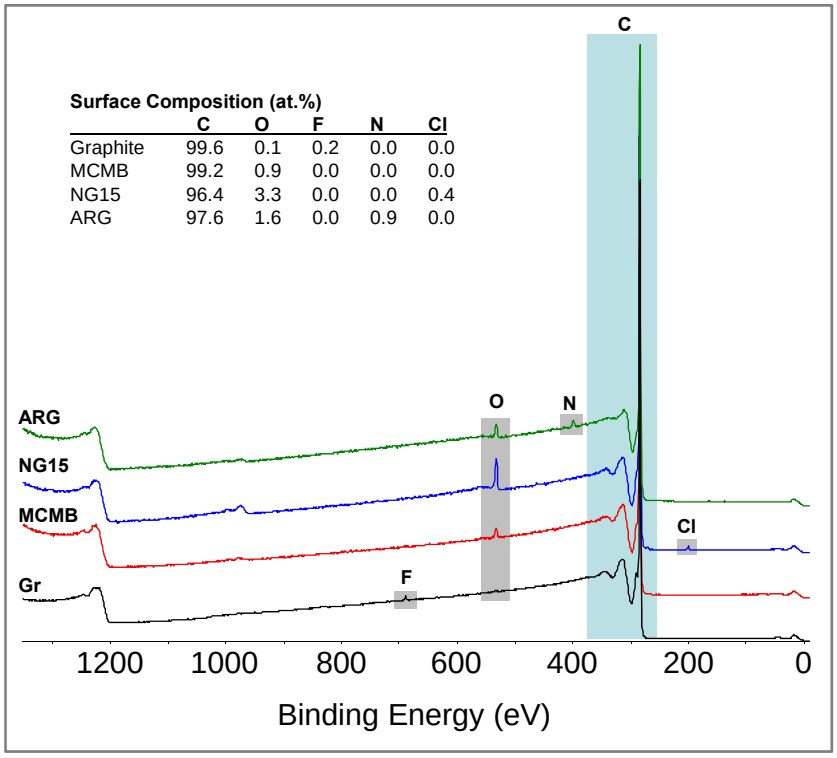

Figure 2. XPS of three untreated graphite samples showing different O and N surface concentrations.

Figure 3 shows Raman spectroscopy results for the ratio of the disordered band (D) to the graphitic band (G) of natural graphite samples heat treated to different temperatures. It is interesting to note that the D/G ratio, which should be ~0.2 for ideal lithium ion intercalation, of the "NG15-H1" and "NG15-H2" samples (both treated to the lowest temperature) is only about 2× that of "NG15-H5" (treated to about double the temperature). These D/G ratios are also comparable to the MCMB baseline material, indicating that the low heat-treatment temperatures of the natural graphite are giving the desired degree of crystallinity. Table 2 shows corresponding XRD data, which breaks down the crystalline structure composition of the natural graphite samples into the hexagonal and rhombohedral phases. It is seen that the weight fraction of hexagonal structure does not change appreciably from the untreated "NG-15" material until the temperature of the "NG15-H5" sample. The point at which no measureable D band in the Raman spectroscopy data occurred, indicating high degree of graphitic structure, was sample "NG15-H7 (second highest temperature investigated) and corresponded to 80.0 wt% hexagonal phase obtained by XRD. It is believed that a majority of the crystallinity should be hexagonal for optimal lithium ion intercalation and that can be achieved with little or no heat treatment.

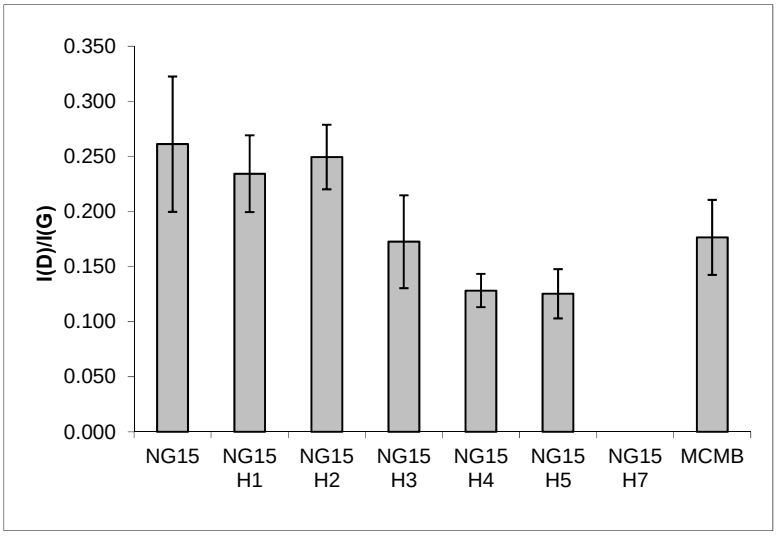

Figure 3. Raman spectroscopy data for natural graphite samples heat-treated to various temperatures compared to MCMB baseline.

Extensive SEM and TEM characterization was completed on the uncoated and carbon-coated, natural graphite heat-treated samples. Particle size and grain size was determined for the samples treated to 950°C, 1050°C, and 2600°C. Figure 4 shows an SEM image of sample "NG15-H8" (maximum temperature investigated) where the smallest crystallites and grain boundaries of the largest crystallites can be seen (denoted by yellow boxes). Extensive surface features were also observed, which increase

Table 2. Crystal structure composition of natural graphite samples heat treated to different temperatures as compared to untreated material (NG-15).

Sample ID	wt% Hexagonal	wt% Rhombohedral
NG-15 (Untreated)	69.7	30.3
NG15-H1 (950°C)	68.2	31.8
NG15-H2 (950°C)	69.5	30.5
NG15-H3 (1200°C)	69.5	30.5
NG15-H4 (1450°C)	70.4	29.6
NG15-H5 (1700°C)	73.2	26.8
NG15-H7 (2300°C)	80.0	20.0

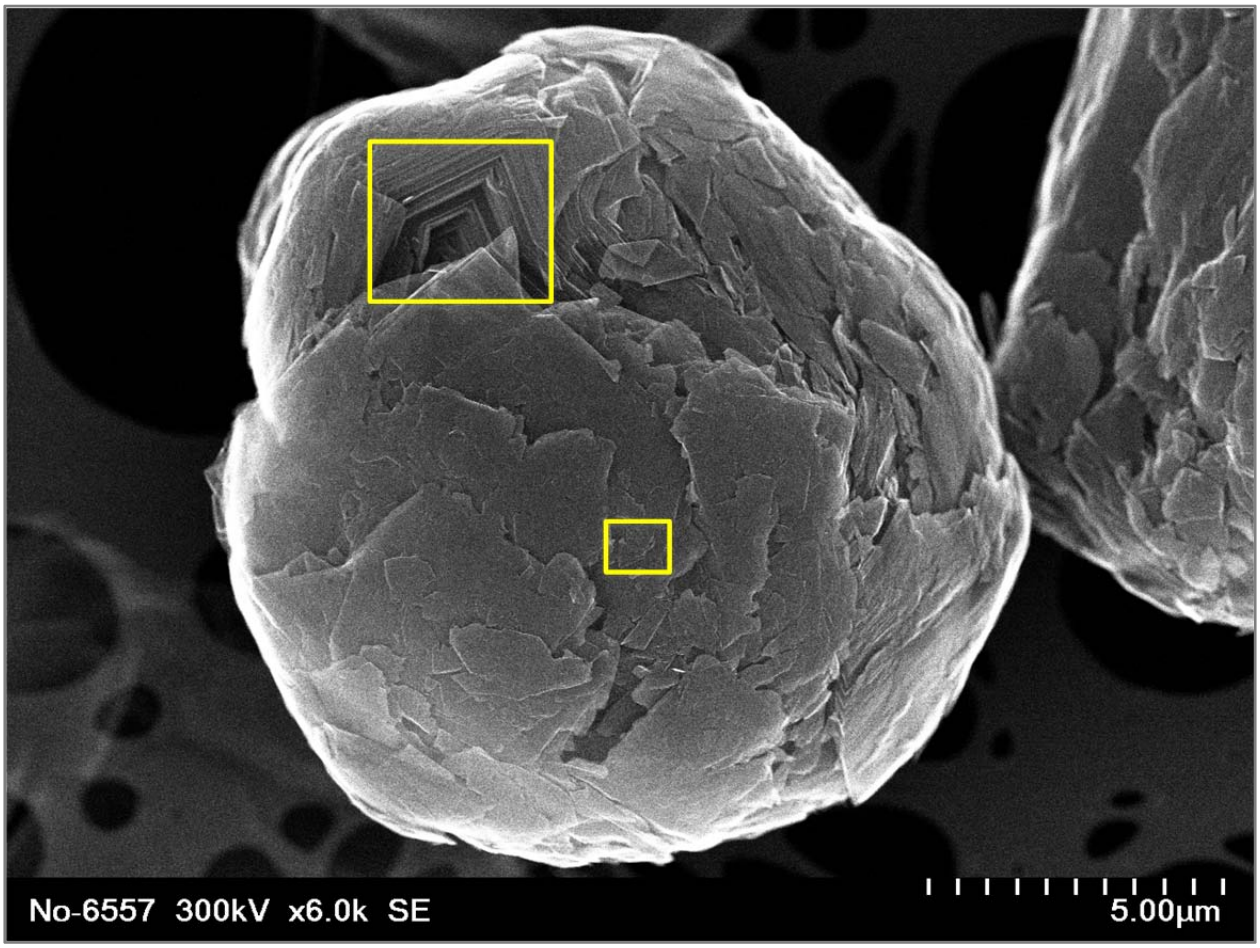

Figure 4. SEM image of natural graphite showing smallest and largest crystallites (indicated by yellow boxes).

the particle surface area. This increase could play a role in forming the solid electrolyte interface (SEI) layer and increase irreversible capacity loss.

A fourth set of natural graphite powders modified with a hard carbon surface coating were heat-treated, and were the primary focus of R&D activities during fall 2010 in addition to the mesophase-pitch surface modified natural graphite already processed. The heat-treatment temperatures of choice were further narrowed to 1050°C and 2000°C after thorough materials characterization and coin cell testing. It was determined through sophisticated TPD-MS experiments that all heat-treated samples undergo surface re-oxidation (i.e., release of H_2O, CO, and CO_2 species), even up to 2600°C, after longer periods of time when exposed to ambient conditions. The TPD-MS experiments showed that no surface re-oxidation occurs through four days of exposure to air after heat treatment to 1000°C in an inert atmosphere. A plan was developed to prevent this surface re-oxidation process through exposure of the powders during the furnace cooling stage to forming gas (4% H_2 in Ar).

XPS results for one of the surface coated natural graphites are shown in Figure 5. It is seen that the heat treated samples ("M1H1" to "M1H4") exhibit about half the amount of chemisorbed (i.e. CO or CO_2) or physically adsorbed (i.e. H_2O) oxygen than the untreated sample ("M1"). It is thought that this oxygen is not present immediately after heat treatment, but instead reacts with the carbon surface over periods of ambient exposure. The crystallographic features of the mesophase-pitch coated and uncoated anode powders were found to vary. XRD results for the hexagonal and rhombohedral compositions were determined for the uncoated natural graphite and the natural graphite coated with mesophase pitch, and the results are shown in Table 3. It is seen that for the lower heat treatment temperatures, the natural graphite coated with mesophase pitch has a higher degree of hexagonal phase than its uncoated counterpart. Higher hexagonal phase composition could be more favorable to intercalation kinetics, especially at the particle surfaces. However, verification of this hypothesis is still ongoing.

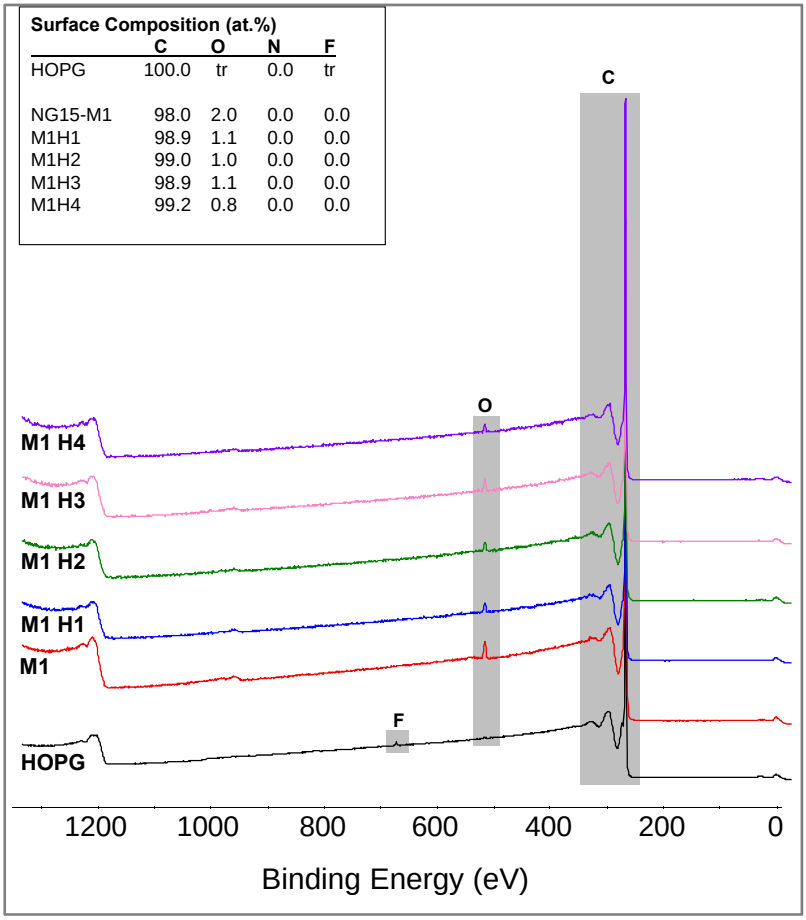

Figure 5. XPS data for natural graphite anode powders coated with carbon showing similar surface oxygen concentrations for heat-treated samples.

Extensive SEM characterization was completed on the natural graphite samples modified with mesophase pitch, and an image for a sample treated to 1050°C is shown in Figure 6. The coating was found to be uniform, and no sharp edges were observed along the particle perimeter. Half-cell data was acquired with all of the heat-treated, uncoated natural graphites and those with the mesophase-pitch coating. Figure 7 shows the reversible capacity performance data taken at C/5 discharge rate for the MCMB baseline and three other samples from this CRADA. It is seen that the natural graphite with no surface coating (unmodified) substantially outperforms the baseline when processed to either temperature (950°C or 2600°C). Modified natural graphite heat treated to 1050°C was also found to outperform unmodified natural graphite heat treated to 2600°C at low C rates (C/5). It was, therefore, demonstrated that certain natural graphite materials can be heat treated to much lower temperatures (<1200°C) and retain their electrochemical properties.

Table 3. XRD results for different heat-treated anode powder samples with and without a mesophase-pitch carbon coating.

Temperature (°C)	Uncoated Anode (Hexagonal/Rhombohedral) %	Coated Anode (Hexagonal/Rhombohedral) %
950	63/37	67/33
1050	NA	66/34
1200	65/35	67/33
1450	67/33	NA
1700	70/30	NA
2000	73/27	73/27
2300	75/25	NA
2600	82/18	NA

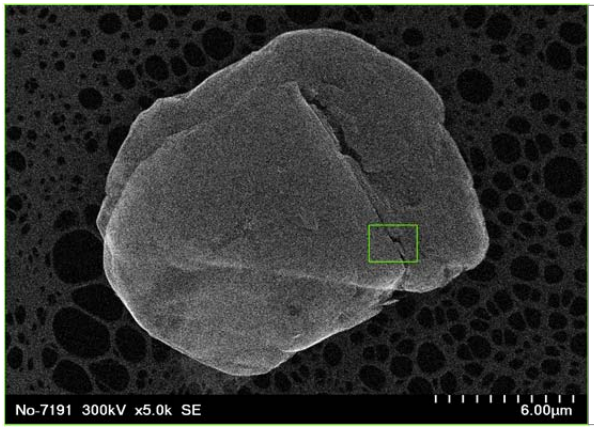

Figure 6. SEM image of (modified) natural graphite coated with mesophase pitch showing smooth coating surface.

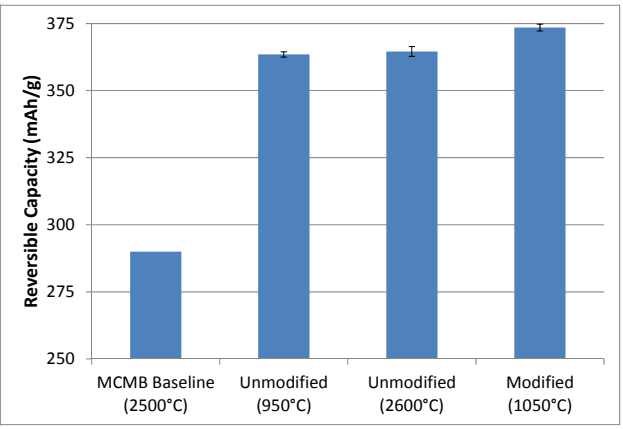

Figure 7. Half-cell irreversible discharge capacity for different heat-treated samples as compared to MCMB baseline (heat treated to 2500°C).

Higher first cycle efficiency and reversible capacity were obtained in half cells with selected natural graphites at much lower heat-treatment temperatures than the MCMB baseline. First cycle efficiency

and reversible capacity was further boosted by implementing a forming gas treatment (4% H_2 in Ar) during sample cooling at ≤900°C, as shown in Figure 8. This treatment is commonly used in the carbon/graphite industry for surface modification and chemically reduces the oxygen containing groups such as carbonyls, quinones, carboxylic acids, etc. and makes the graphite surface much more hydrophobic. It is not clear at this stage why this surface change is beneficial to performance, but it could have to do with formation of a more chemically stable anode solid electrolyte interface (SEI) layer

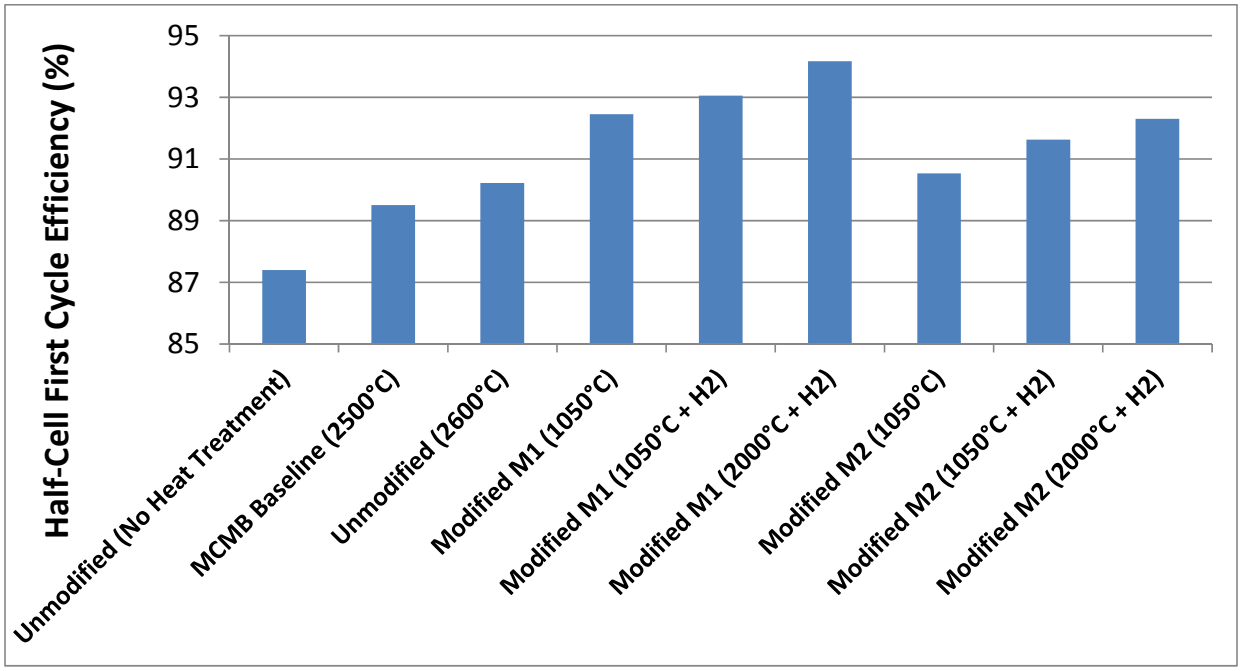

Figure 8. Half-cell first cycle efficiencies of various anode heat-treated graphite powders.

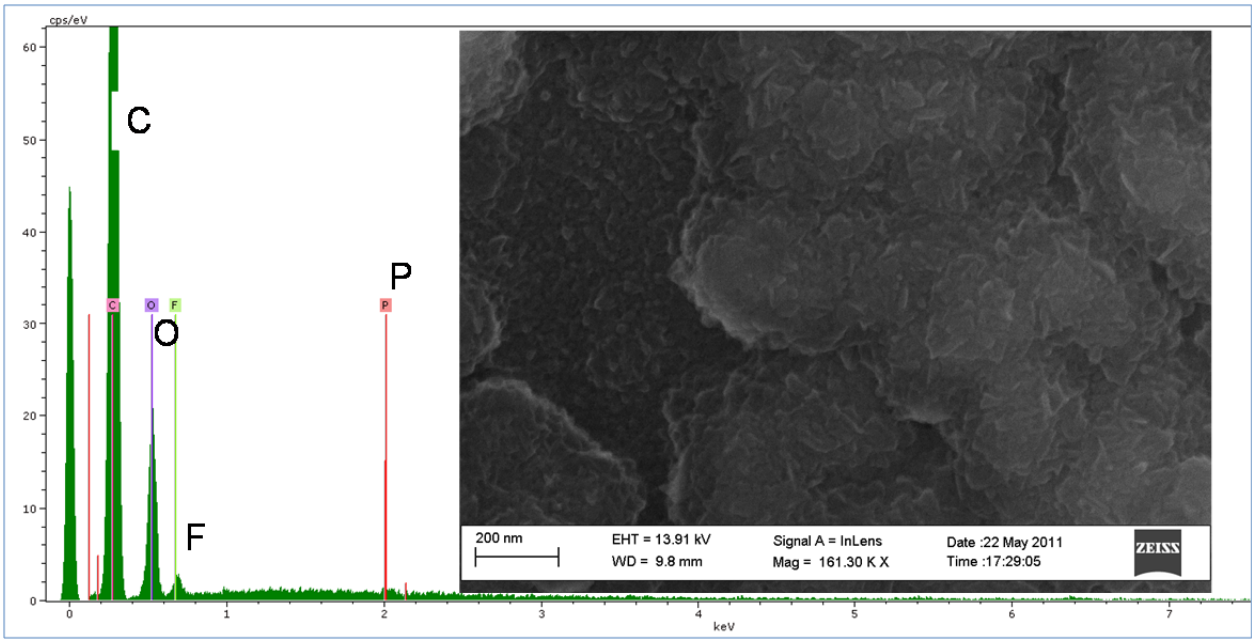

Figure 9. SEM micrograph and corresponding EDS spectrum for a cycled lithium ion battery anode natural graphite material showing the chemical and structural features of the SEI layer.

and improved lithium ion transport at the solid-liquid interface. SEM and EDS analysis of a typical anode SEI layer are shown in Figure 9 for a natural graphite material *without* the forming gas treatment. The EDS spectrum suggests electrolyte decomposition compounds such as LiF, Li_2CO_3, POF, and polycarbonate on the surface of the graphite. XRD data has been obtained for natural graphite that has been processed with and without forming gas treatment, which confirms there is no microstructural or crystallographic changes to the graphite after exposure to forming gas.
During winter 2011, this initial performance gain *without* H_2 treatment did not translate into durability improvement, as 75-85% capacity fade was measured through 100 coin cell cycles at a 1C/2C charge-discharge rate (compared to the 20-30% baseline). Optimization of the aqueous electrode dispersions for the new graphites, longer dwell times at maximum heat-treatment temperature, and a longer exposure time to the forming gas was found to improve durability.

By fall 2011, optimization of the anode graphite powder heat-treatment process was nearly completed, and batch sizes were scaled from 100 g to 4 kg. Through optimization of the furnace gas chemistry (4% H_2 in Ar or N_2), first cycle efficiency, reversible capacity, and capacity retention was improved by switching from H_2 exposure during sample cooling only to H_2 exposure during the entire heat treatment protocol. Two different natural graphite samples (unmodified NG15 and surface modified NG15-M2) were processed in both furnace environments, including 4 kg batch sizes of NG15, and results through 1000 1C/-1C charge-discharge cycles were acquired (see Section 5.3).

As a surface characterization technique, XPS gives an estimate of the chemical composition of several uppermost layers of material (about 15-20 nm in depth). This information may be useful for characterization of carbon fibers or carbon/carbon composites, but it may be misleading for characterization of surface chemistry on anode graphite materials. Indeed, the SEI layer is formed from the interaction of electrolyte with the outermost surface of graphite particles. Only those oxygenated surface groups located in surface chemical groups on the exposed graphite surface, presumably at the edge carbon atoms of graphene sheets, participate directly in formation of the SEI layer. This "electrochemically active" oxygen is better characterized by the TPD-MS technique. The method is based on detection by mass spectrometry of gas species (H_2O, CO_2, CO) formed by thermolysis of surface groups and released to the carrier gas (He). In a non-porous material such as graphite, these gas species originate in the outmost surface of graphite grains and therefore they better represent the local chemical environment on the exposed graphite surface. In addition, the TPD-MS technique allows for qualitative assessment of the nature of surface chemical groups based on the decomposition temperature and the nature of gas released, along with quantitative estimation of their concentration from the integrated area of decomposition peaks. It was shown that oxygen concentrations calculated from XPS, TPD-MS, and elemental analysis follow a similar trend, but do not match quantitatively the XPS values, which in general are higher than the other results.

TPD-MS analysis of surface functional groups on untreated and surface-treated graphite was done using an Autosorb 1C instrument (Quantachrome Instruments) equipped with quadrupole mass spectrometer (Pfeiffer). About 150 mg of graphite powder was placed in a U-shaped quartz tube and flushed with high purity helium. After stabilization of the flow and of mass spectrometer signals, a linear heating ramp (10

°C/min) was applied from room temperature to 1000 °C. The mass spectrometer signals for H_2O, CO_2, and CO were continuously recorded. The peaks versus time (or temperature) were integrated and compared with separate experiments on decomposition of calcium oxalate which were used for quantitative calibration.

Figure 10 shows H_2O emission TPD-MS data for the NG15 unmodified natural graphite samples with various gas treatments during processing. It is seen that all gas treatments with 4% H_2 result in low adsorbed water on the graphite powder surface, but the treatment with 4%H_2/N_2 for the entire protocol has the lowest H_2O emission. This surface chemistry characterization confirms that the graphite surfaces are much less hydrophilic (hydroxylated or chemisorbed water) after each heat treatment protocol and also correlates well with the fact that fewer carboxyl, lactone, quinone, etc. (hydrophilic) groups were measured on the graphite surfaces via TPD-MS.

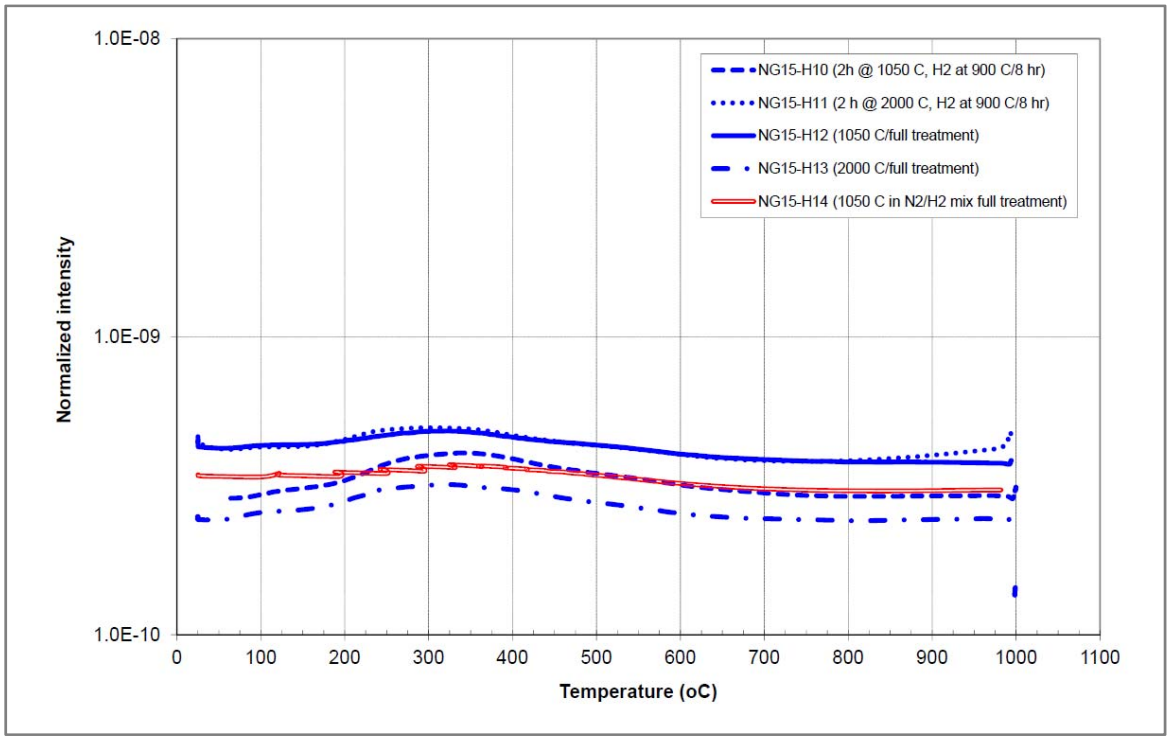

Figure 10. TPD-MS analysis of adsorbed water emission from several different natural graphite anode powders heat-treated under different conditions. NG15-H10 to NG15-H13 were treated with an Ar diluent and NG15-H14 was treated with a N_2 diluant (all samples were treated in 4% H_2).

A synoptic presentation of TPD-MS results is shown in Figure 11. In this figure the samples are arranged according to the treatment applied (IA = inert atmosphere; E1 to E3 = surface treatments with controlled gas composition) and the treatment temperature. The same template is used in Table 4, which summarizes the amounts of released gases (H_2O, CO_2, CO) measured in TPD-MS runs. The amounts (calculated in wt % relative to the initial graphite weight) were calculated by integrating the peaks shown in Figure 11 and using previously calibrated sensitivity factors. These results support the following quantitative observations:

- The surface of untreated natural graphite (NG15) is reach in surface groups that release water, CO_2 and CO. The assignment of TPD-MS peaks to various chemical functionalities on carbon surface is not unambiguous, as the peak temperature may vary with the heating rate and depends on the texture of materials. In the following discussion we used the work by Figueiredo et al. for guidance. A small amount of physisorbed water is released below ~150°C. Larger amounts released together with CO_2 between ~200 and ~500°C originate from thermolysis of carboxylic groups. Decomposition of anhydrides generates CO and CO_2 between ~400 and ~600°C. The CO release at higher temperatures is associated with thermolysis of phenols and quinones, which continues above 1000°C as well.

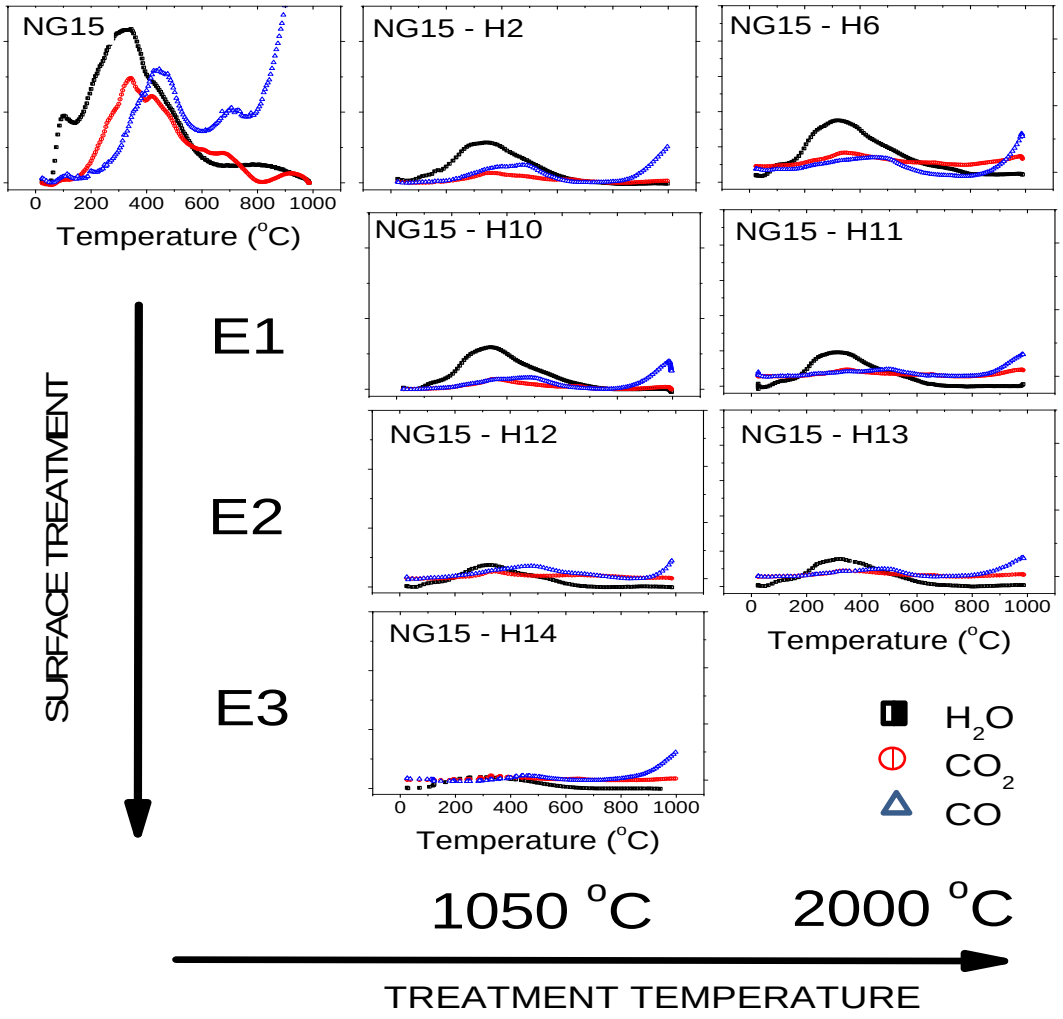

Figure 11. Graphic summary of TPD-MS results. See text for detailed explanation of schematic. Same (arbitrary) units were used in all plots for the MS signals of H_2O, CO_2 and CO.

- Treatment in inert atmosphere greatly diminishes the amounts of oxygenated surface groups that decompose to CO and CO_2 (lactones, phenols, quinones) but does not totally eliminate the

release of water (samples NG15-H2 and NG15-H6). Surface treatment labeled E1 reduces the amount of water released; high temperature conditions have a marginal effect on the amount of surface water (samples NG15-H10 and NG15-H11). In contrast, surface treatments labeled E2 and E3 are even more efficient in further lowering the amounts of surface oxygen (samples NG15-H12 and NG15-H13). In particular, treatment E3 at 1050^{o}C leaves practically a clean graphite surface (sample NG15-H14).

- Surface water is always in larger amount, and is more difficult to remove, requiring gradually more aggressive surface treatments (E2, E3). Obviously, this water has higher binding energy than physisorbed water. In the temperature range where strongly bonded water is released (400 to 600^{o}C) we have always observed hydrocarbon fragments corresponding to C_1 (15 amu), C_2 (26 – 30 amu), and C_3 (39 – 41 amu). The release of these light hydrocarbons (not shown here) is diminished by the same treatments that are effective in reducing the amount of water. It has been previously reported from Somorjai group that adsorption of water graphite thermally cleaned at high temperature causes broad water TPD peaks and small hydrocarbon fragments in the same temperature range. These features were explained by chemisorption on water at reactive edge carbon atoms and breaking of carbon-carbon bonds linking isolated aliphatic fragments through radical formation and recombination during thermal decomposition. We cannot rule out the possibility that water chemisorption occurred during the short exposure to ambient of the highly reactive surface of thermally treated graphite. This explains why chemisorbed water is in larger amounts than carbon oxides, and why more aggressive surface treatments (E2, E3) are more efficient in blocking water chemisorption.

Table 4. Quantitative summary of TPD-MS results showing surface concentrations (wt%) of H_2O, CO_2 and CO released from treated samples.

	NG15	**NG15-H2**	**NG15-H6**	
IA	1.072	0.22	0.342	H_2O
	2.307	0.057	0.099	CO_2
	1.533	0.062	0.126	CO
SURFACE TREATMENT		**NG15-H10**	**NG15-H11**	
	E1	0.242	0.19	H_2O
		0.063	0.046	CO_2
		0.105	0.049	CO
		NG15-H12	**NG15-H13**	
	E2	0.147	0.159	H_2O
		0.013	0.04	CO_2
		0.085	0.058	CO
		NG15-H14		
	E3	0.063		H_2O
		0.025		CO_2
		0.042		CO
TEMPERATURE		*1050^{o}C*	*2000^{o}C*	

In summary, quantitative analysis of TPD-MS results show that the amount of oxygen-containing surface groups can be reduced more efficiently by controlling the chemical environment during thermal treatment at 1050^{o}C. Water readsorption occurs easier than reoxidation at ambient temperature, but blocking water chemisorption is possible with a suitable selected gas composition during thermal treatment.

5.2. Description of Final Heat-Treatment Protocol

The novelty of this processing methodology is that it combines a low-temperature heat-treatment protocol for natural graphite with a gas-phase surface treatment that changes the graphite surface chemistry from hydrophilic (oxide and water containing) to hydrophobic (limited oxide and water content). The maximum heat-treatment temperature required is only 1050°C and exposes the graphite powder to forming gas (4% hydrogen in argon) either during the entire heat-treatment protocol or just the cooling portion. This reduced temperature results in substantial processing energy savings. A further benefit is that the argon could be replaced with nitrogen because the maximum heat-treatment temperature is only 1050°C, resulting in even greater savings for the anode graphite powder processing step. Graphite powders subjected to this heat treatment process have shown in full coin cells vastly superior long-term performance (capacity fade) to their counterparts without the forming gas surface treatment (see Section 5.3). In addition, the first-cycle coulombic efficiency in half cells was also increased due to improved surface interactions between the solid graphite and liquid battery electrolyte that forms the SEI layer.

The processing method takes a natural graphite and subjects it to a heat-treatment protocol that must include exposure to forming gas (4% hydrogen in argon). The surface chemistry is optimized during the process for a lithium ion battery anode, and the maximum heat-treatment temperature required is reduced from 2500°C to 1050°C. For this invention to provide the desired results, the natural graphite must have the correct specific properties and may have a surface coating of amorphous carbon.

The anode graphite powder is first loaded into a furnace in a graphite crucible at room temperature. The temperature is ramped up to the maximum value (i.e. 1050°C) at 10°C/min and held at the maximum temperature for 2 h. After the 2-h hold, the furnace is allowed to cool to 900°C, at which point the forming gas (4% hydrogen in argon) is introduced. The temperature is held at 900°C for 2-8 h to allow conversion of the surface chemistry. After the second hold at 900°C, the furnace is allowed to cool to room temperature with the graphite powder exposed to forming gas.

An alternative protocol is to perform the entire heat treatment with forming gas to save on processing energy costs. The anode graphite powder is first loaded into a furnace in a graphite crucible at room temperature. The temperature is ramped up to the maximum value (i.e. 1050°C) at 10°C/min and held at the maximum temperature for 2 h. After the 2-h hold, the furnace is allowed to cool to room temperature with the graphite powder exposed to forming gas.

A further important alternative is to use a custom blend of 4-10% hydrogen in nitrogen as a substitute for the forming gas (4% hydrogen in argon) portions of the heat treatment protocol. This would add

even more cost savings to the heat treatment process and potentially further improve long-term performance of the anode during cell operation.

5.3. Anode Performance and Cycle Life

The efficiency improvement shown in Figure 8 (Section 5.1) for the modified M2 translated into superior long-term charge-discharge (1C/2C) cycling for full coin cells as shown in Figure 12 (obtained in summer 2011). It can be seen that the sample with forming gas treatment during furnace cooling (NG15-M2-H3) far outperforms the sample without treatment, and nearly equals the performance of the A123 standard synthetic graphite. This data shows that similar long-term performance can be achieved with a modified natural graphite and forming gas treatment at heat-treatment processing temperatures approximately 1500°C lower than for the synthetic graphite samples. Figure 13 shows CO_2 emission TPD-MS data for the M2 modified natural graphite samples with various forming gas treatments during processing compared to without the forming gas treatment. It can be seen that regardless of the type of treatment with forming gas, the CO_2 emission is much lower than for the sample without forming gas treatment (NG15-M2-H1). This surface chemistry characterization confirms that there are substantially fewer carboxyl, lactone, quinone, etc. groups on the surface of the natural graphite after forming gas treatment.

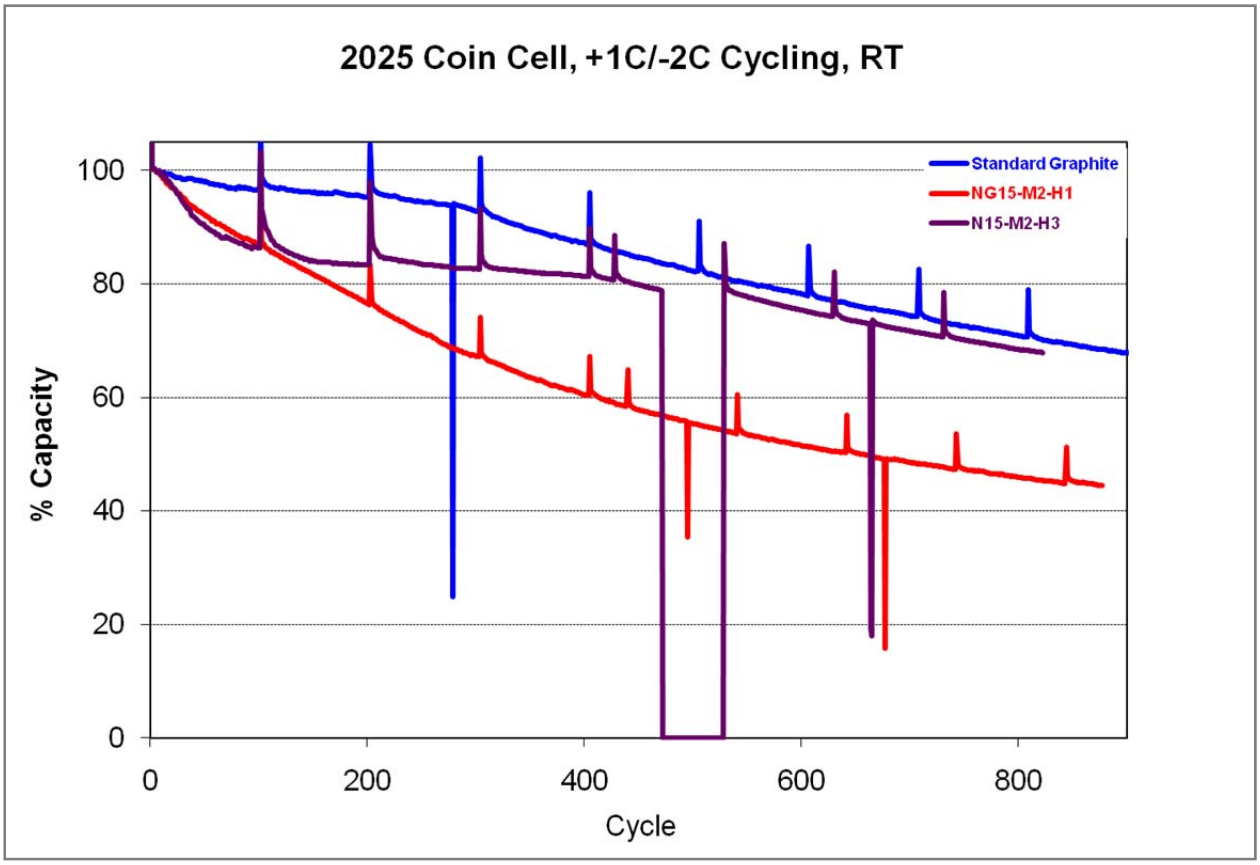

Figure 12. Comparison of long-term charge-discharge cycling of M2 modified natural graphite with (NG15-M2-H3) and without (NG15-M2-H1) forming gas treatment during furnace cooling compared to A123 synthetic graphite baseline.

Figure 14 shows excellent long-term performance data for full coin cells with two different natural graphites – the unmodified NG15 and the surface modified NG15-M2. The coin cells with the different

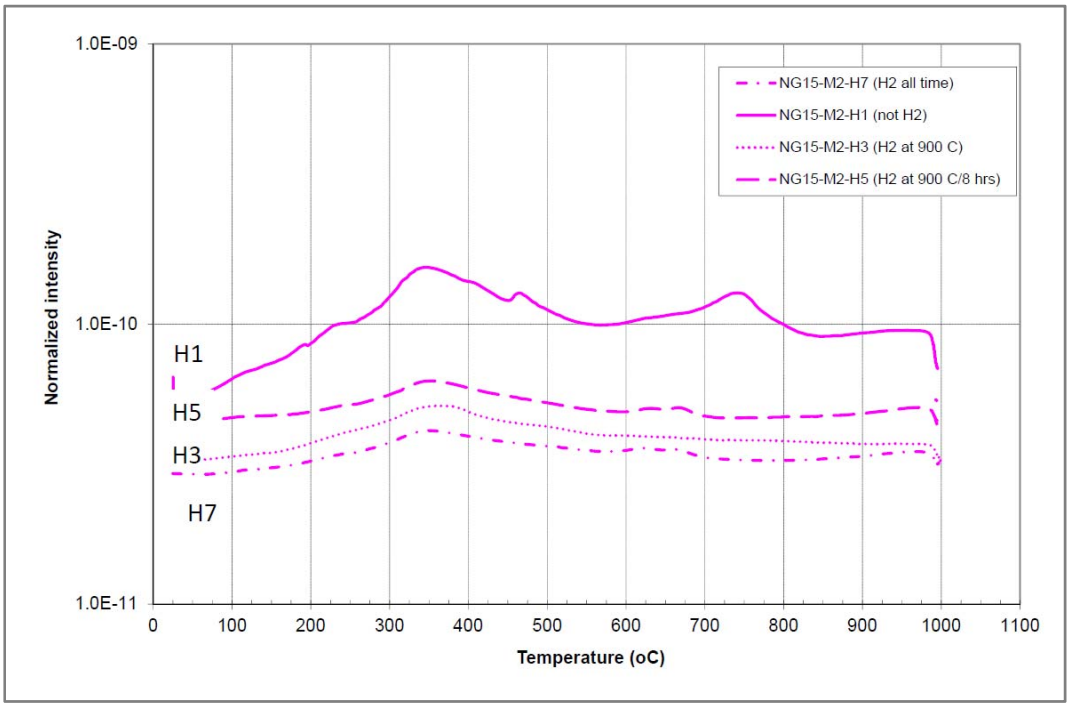

Figure 13. TPD-MS data for CO_2 emissions from the surfaces of different modified M2 natural graphite samples showing much lower emissions for samples treated with forming gas.

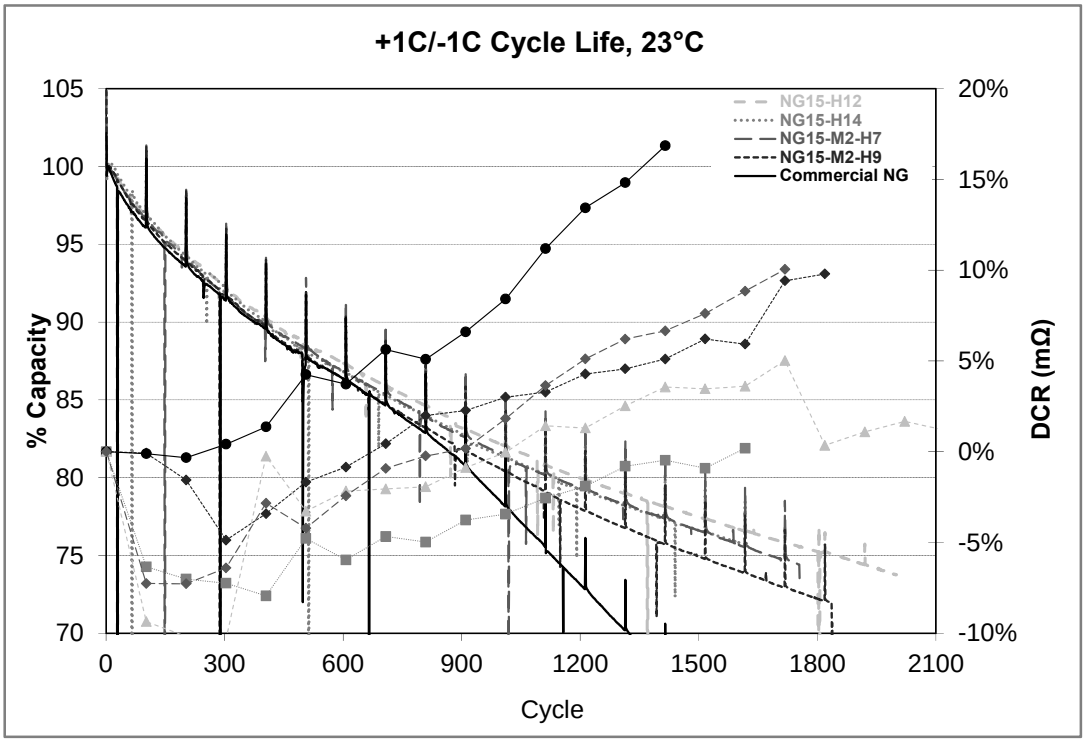

Figure 14. Long-term performance of 4% H_2 (in either N_2 or Ar diluent) treated anodes in full coin cells compared to commercial natural graphite baseline.

gas chemistries treated up to 1050°C – either 4% H_2 in Ar (NG15-H12 and NG15-M2-H7) or N_2 (NG15-H14 and NG15-M2-H9) – all have 72-75% capacity retention after 1600-2000 cycles and significantly outperformed the baseline natural graphite.

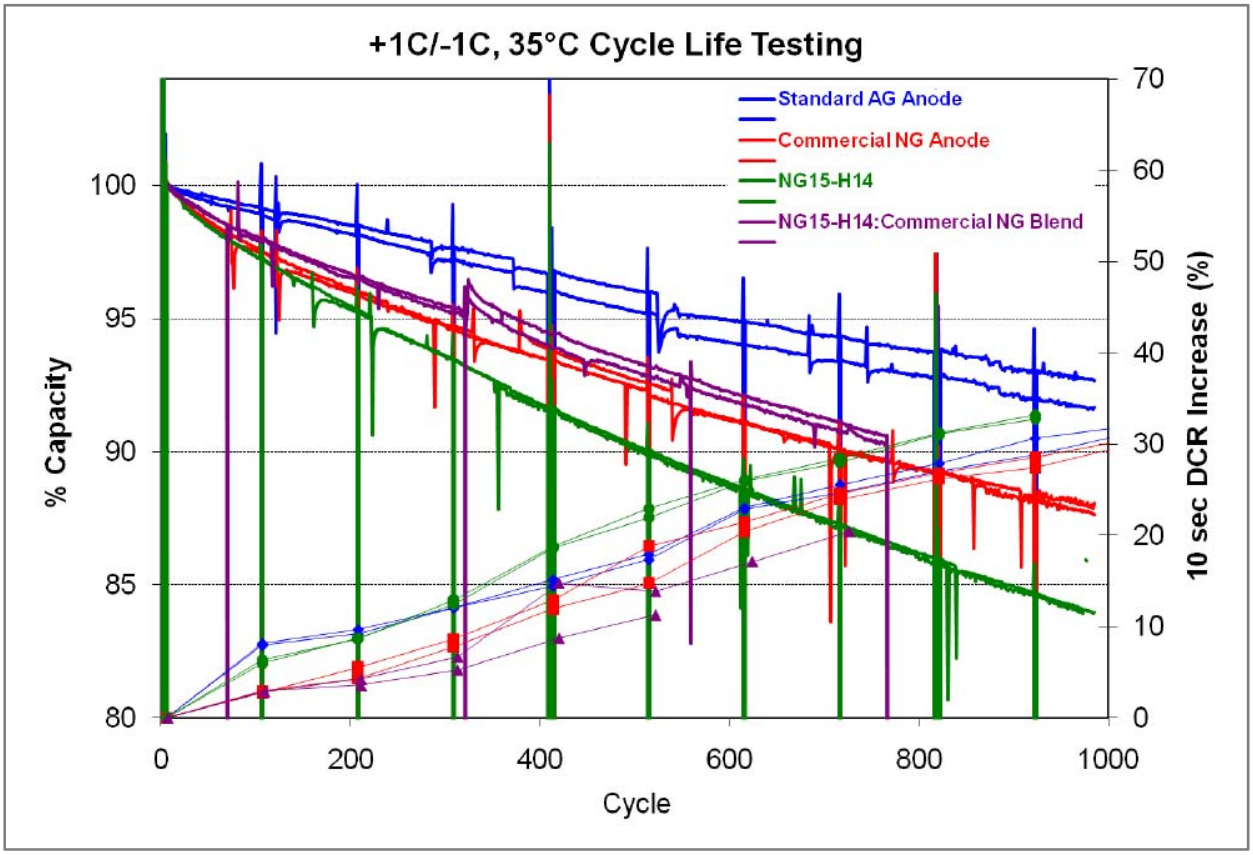

Figure 15. Full-active-area, pouch-cell long-term cycling of NG15-H14 (4% H_2 in N_2 treatment) and 70/30 wt% NG15-H14/commercial NG blend with scaled 7-8 kg batch size produced at ORNL compared to A123 commercial NG and AG baselines.

The anode graphite powder heat-treatment process was successfully scaled from 100 g to 7-8 kg for both gas environments – 4%H_2/N_2 and 4%H_2/Ar. Through this optimization of the furnace gas chemistry, we improved first cycle efficiency and capacity retention by switching from H_2 exposure during sample cooling only to H_2 exposure during the entire heat treatment protocol. Two different natural graphite samples (NG15 and NG15-M2) were processed in both furnace environments at the 7-8 kg scale, and results through 1600-2000 1C/-1C charge-discharge cycles were acquired. Based on these successful full coin cell durability tests, large-format pouch cells were constructed with NG15-H14 (4% H_2 in N_2 treatment) and tested for 700-850 1C/-1C cycles using the scaled 7-8 kg anode powder batch. Two anode formulations, a pure NG15-H14 anode and a 70/30 wt% NG15-H14/commercial NG blend, were tested against the commercial natural graphite (NG) and artificial graphite (AG) baselines. This durability data is shown in Figure 15. The best performance was seen with the AG baseline, which had 7% capacity fade through 850 cycles, followed by the blend, which had 9% capacity fade through 700 cycles. ORNL believes that the performance of the pure NG15-H14 anode, which exhibited 13% capacity fade through 720 cycles, would be better with an optimized crucible design allowing the 4%H_2/N_2

mixture to penetrate the powder depth more evenly. A US patent application has been filed for this heat-treatment process, which specifies that the effect of deleterious H_2 concentration gradients be eliminated during treatment (i.e., employment of a rotary kiln, etc.).

6. Subject Inventions

The developed processing technology, which significantly reduces maximum heat-treatment temperature and thermal budget by utilizing a controlled furnace gas environment with reducing atmosphere, was submitted as an ORNL invention disclosure. A non-provisional patent application was subsequently drafted and submitted on 8/20/12 (U.S. Patent Application No. 13/596,291).

7. Commercialization Possibilities

This technology could be commercialized as a new low-cost anode material for lithium ion batteries. The initial target market would be large format cells for transportation. A123's Livonia, MI cell assembly plant represents a demand of 530 MT/year of anode material at the designed 20 cell per minute production capacity. At $7/kg, this corresponds to $3.7M captive market. The global demand for lithium ion batteries is strongly driven by the price of oil, ranging from a conservative 6000 MWh to optimistic 20,000 MWh in 2020, which translates to a total anode material demand of 5000 to 16,500 MT/yr in 2020. With the growth of transportation and grid energy storage as a market segment, the downward cost pressure will be intense. Thus A123 Systems projects that the majority of the commercial cell market, including batteries for consumer electronics, will be available to a low-cost anode that meets or exceeds today's state of the art engineered, artificial graphite materials.

8. Plans for Future Collaboration

A123 Systems and ORNL have recently submitted a proposal under the AMO Innovative Manufacturing Initiative that provided a detailed plan to develop and manufacture lithium ion battery anode materials at a 60% cost reduction versus the state of the art anodes used in vehicle and grid energy storage applications. It is intended to continue this collaboration at a rate comparable to available funding. Since the present level of internal R&D support at A123 Systems is limited, A123 Systems will continue to work with ORNL to seek additional funding for scale up of the anode processing technology from this CRADA.

9. Conclusions

Over the course of this project, an anode raw material heat-treatment protocol was developed that optimizes thermal budget and reduces maximum treatment temperature for natural graphite materials. ORNL focused on advanced materials characterization and heat-treatment protocol development and scale-up, while A123 Systems focused on electrochemical characterization, cell testing, and protocol validation. The maximum heat treatment temperature was reduced from well over 2000°C for synthetic graphite anodes such as mesoporous carbon microbeads (MCMB) to 1050°C with 4% H_2 addition to the furnace inert gas environment, which translates into 40-50% reduction in thermal budget (assuming 10°C/min ramp time and two 2-h temperature holds for the treatment above 2000°C). U.S. Patent Application No. 13/596,291 covering this technology was filed on 8/20/12 with joint inventors and assignees between ORNL and A123 Systems.