ORNL Manufacturing Demonstration Facility
Technical Collaboration **Final Report**

Feasibility Demonstration of Graphene-Based Lithium Batteries with Enhanced Charge Rate and Energy Storage Capacity[1]

Vorbeck Materials Corp.

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Company Size: Small business

Summary
Vorbeck Materials Corp. and ORNL partnered to demonstrate the compatibility of Vor-x® graphene in existing roll to roll manufacturing processes, and the feasibility of Vor-x® graphene to improve the recharge rate in existing Li-ion battery chemistries. In full coin cell tests NMC (Lithium nickel manganese cobalt oxide)/graphene cathodes demonstrated a 7% improvement in discharge capacity at 1C and a 200% improvement at 5C compared to NMC/carbon black. NMC/graphene slurries demonstrated short shelf life which limited the team's ability to demonstrate these improvements in pouch cells. The projects results provided valuable information to Vorbeck for their next development step to make slurries more stable and to allow the technology to be tested in future efforts.

Background
Long recharge time is a significant challenge facing batteries for portable applications. There is a large asymmetry between the discharge rate and the charge rate of almost all Li-ion battery systems. Most manufacturers rate the power of the battery based on the discharge rate while the charge rate is four to ten times slower. This not only impacts the time spent connected to an outlet to recharge the battery, but it also significantly curtails energy recovery from high-output sources. Vorbeck has been working to develop electrode materials that enable improved battery cost, capacity and recharge rates through the use of Vorbeck's Vor-x® graphene. Graphene possesses very high electrical and thermal conductivity, and with low percolation thresholds that can uniquely provide uniform current and heat distributions in electrodes with minimal loading when distributed properly. ORNL's MDF has provided battery processing and

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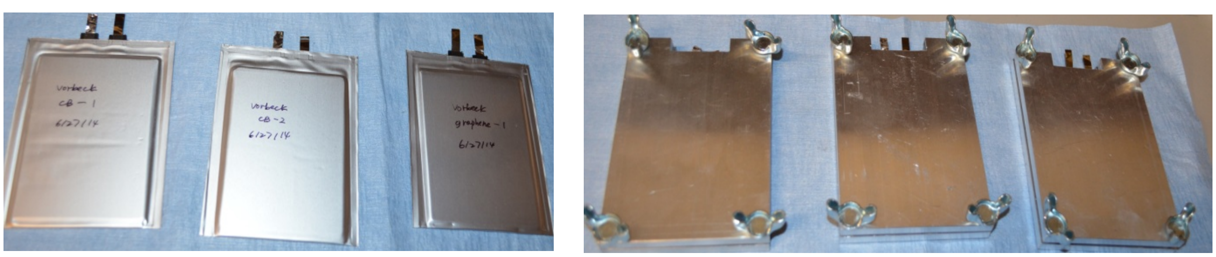
scale-up guidance to major industrial manufacturers. The team has unique battery piloting expertise and equipment to allow demonstration of the new Vor-x® graphene-based electrode materials on a practical scale. ORNL and Vorbeck have teamed to produce pouch cells utilizing this innovative graphene battery technology to demonstrate the advantages and manufacturability of graphene-based batteries.

Technical Results

Vorbeck Materials provided ORNL with premixed NMC/graphene and NMC/carbon black (CB) samples. The samples were diluted with N-methyl-2-pyrrolidone (NMP) to obtain appropriate viscosity for slot-die coating at the MDF. The two cathode materials were assembled into full coin cells. All three cells show good rate performance and align with results obtained at Vorbeck Materials. Replacing CB with graphene dramatically improved the rate performance. For example, the NMC/graphene cells demonstrated ~145 mAh/g discharge capacity when being discharged at 1C, compared to the ~135 mAh/g from the NMC/CB, corresponding to ~7.4% improvement. The improvement was more significant at higher C-rate, such as 17 mAh/g at 5C, and 53 mAh/g for NMC/CB and NMC/graphene, respectively, corresponding to more than 200% improvement. All three cells exhibited excellent Coulombic efficiency.

Cathode materials were also assembled into pouch cells for testing (Figure 1). Because of the limited amount of cathode material which was able to be effectively cast with the slot die coater, only a single pouch cell was successfully constructed with NMC/graphene. The pouch cells with carbon black and graphene were characterized for their rate performance. The cells were charged at C/5 to 4.2 V followed by constant voltage charging at 4.2 V until $I \leq$ C/20 and then discharged at various C-rates. For comparison, the discharge capacity was normalized to their theoretical capacities. Figure 2 shows rate performance results. The two NMC/CB cells showed excellent rate performance and were almost identical to ORNL baseline cells. The NMC/CB cells were also very consistent showing good reproducibility in electrode coating and cell assembly. The one NMC/graphene cell demonstrated higher capacity retention than the NMC/CB cells up to C/2, but suffered dramatic drop in capacity at high rates. This is not in agreement with the coin cell results. All three pouch cells showed comparable capacity when cycled at 1C/-2C at the end of rate test to that when cycled at 0.2C/-2C during the rate test.



a) b)

Figure 1. NMC/CB and NMC/graphene pouch cells a) individual pouch cell and b) test units

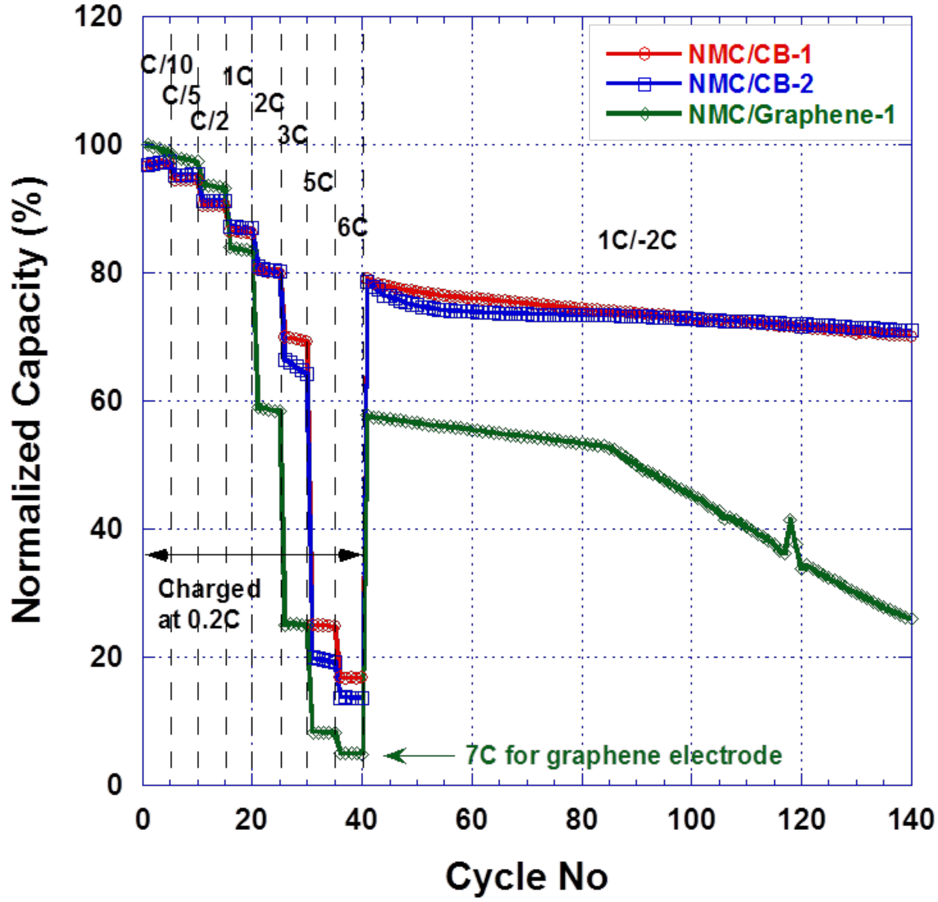


Figure 2. Rate performance of NMC/CB and NMC/graphene pouch cells

Further testing of NMC/graphene was limited by stability issues of the graphene-bearing cathode slurries. These slurries were found to gel and thus were not amenable to the dispersion with NMP which is necessary for the coating process. It is suspected that the issue may be caused by adsorption of moisture. Onsite mixing of the cathode pigment material and PVDF (polyvinyl-di-fluoride) powder at ORNL did not resolve the issue as loadings of the material in these coatings were insufficient for comparison to the NMC/CB coatings used in the coin cell tests which had much higher loadings.

Impacts

Commercialization of the graphene battery technologies will enhance the economic and energy security of the US through (1) reduced energy imports (diesel-electric hybrids in medium-duty vehicles can result in fuel savings of up to 50%. This will make hybrids, in general, more attractive to fleet operators and increase adoption), and (2) reduced emissions from medium-duty vehicles (for every 100 additional hybrid medium-duty fleet vehicles adopted, a savings of ~ 50,000 gallons of fuel and 525 metric tons of CO_2 occurs). In the long-term, these improvements could also be applied to passenger vehicles, further increasing the impact. In addition, the project will help maintain U.S. leadership in medium/heavy duty and construction vehicle technology. The improved vehicle batteries will provide superiority in energy storage capacity, recharge rate, cycle life, and cost.

Conclusions
NMC (Lithium nickel manganese cobalt oxide) cathodes were manufactured with carbon black (CB) and graphene as the conductive additives. A limited number of full coin cells and pouch cells were assembled with the two cathode materials. Based on the full coin cells, the NMC cathode with graphene as the conductive additive demonstrated superior rate performance compared to cathodes with CB as the conductive additive. However, this improvement was only found at C/2 and below for the pouch cell, and did not occur at higher C-rates. This result may not be representative since only one NMC/graphene pouch cell was able to be tested as there were difficulties with coating due to gelation of the NMC/graphene/PVDF slurries. Gelation potentially results from moisture entrained during the premixing or transport stages.

Through this program, Vorbeck was able to advance its NMC and LFP (lithium iron phosphate) battery electrode processing capability, and the company was able to have its results reproduced outside of its laboratory. Additionally, Vorbeck gained valuable exposure to the pouch cell production process, facilitating the company in its current development of in-house pouch cell fabrication capability. Vorbeck and ORNL were able to identify technical barriers for scale up. For instance, the sensitivity of the slurry to the time and environment has been noted, and further work is necessary to improve the suitability of Vorbeck's NMC/graphene slurries for slot die coating. The benefits of this project extend beyond the advancement of traditional Li-ion battery technology as they are also being used to promote Vorbeck's Li-S battery development.

About the Company
Vorbeck Materials Corp. is a U.S.-based technology and manufacturing company established in 2006 to develop products using Vor-x®, Vorbeck's patented graphene technology, initially developed at Princeton University. Vorbeck launched the world's first commercial graphene product with the introduction of Vor-ink™, a graphene-based conductive ink for electronics applications.

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