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Hexagonal boron nitride incorporation to achieve high performance Li$_4$Ti$_5$O$_{12}$ electrodes

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ABSTRACT
There is an increasing demand for fast charging and high capacity lithium ion batteries. However, conventional Li-ion battery chemistries cannot meet the stringent requirements of these demands due to the poor performance of graphite anodes, especially on safety during fast charging. Finding the right anode material that can replace conventional graphite while providing high capacity is very challenging. Today, lithium titanium oxide (LTO) is considered one of the most attractive anode materials that can provide the desired ultra-fast charging ability (>10C) with high safety. However, it has many serious drawbacks when compared to the existing graphite anodes, including poor intrinsic conductivity, narrow electrochemical window, etc. Extensive research has been done to overcome these problems, especially in developing new LTO composite materials with reduced graphene oxide. However, even these methods have rapid capacity fading at high current densities, >5C, due to increased internal resistance and polarization losses. Here, we demonstrate an effective way to improve LTO composite materials by developing unique nanoengineered three-dimensional frameworks with hexagonal boron nitride (h-BN) addition. Li-ion cells with h-BN incorporation exhibit excellent performance and operational stability, especially at fast and ultra-fast charging rates, >10C.

Lithium ion batteries (LIBs) have become an integral component of everyday life and power a wide range of commercial products, from small portable electronic devices to electric vehicles.$^{1–3}$ However, conventional state-of-the-art LIB chemistries cannot keep up with the increasing power and fast charging demand from users. Most importantly, they exhibit very poor safety characteristics and even catastrophic failures, such as fire or explosion, at high power applications due to their graphite-based anodes.$^{3–5}$ New or improved battery chemistries are urgently needed to support the future power demand while ensuring safety. Lithium titanium oxide (Li$_4$Ti$_5$O$_{12}$, or LTO) material is considered one of the ideal candidates for next-generation LIBs, as an alternative anode to graphite. LTO has very desirable properties for high power applications, such as a good structural stability due to its zero-strain insertion abilities and resistivity to unwanted solid-electrolyte interphase (SEI) due to its flat charge/discharge potential (ca. 1.5 V vs Li$^+$/Li$^-$).$^{4–8}$ All of these properties make LTO one of the safer chemistries for LIBs. However, LTO displays many serious drawbacks as compared to the existing graphite anodes, including poor intrinsic conductivity (10$^{-9}$ S cm$^{-1}$), lithium ion transfer capability, energy density, and theoretical capacity of 175 mA h g$^{-1}$.$^{9,10}$ To overcome these drawbacks, numerous device architectures have been proposed and studied, including developing alternative surface modifications,$^{11,12}$ bulk doping,$^{13,14}$ and morphological adjustment.$^{15–22}$ Among all these, developing LTO composite structures with other material implementations, especially with reduced graphene oxide (r-GO), widened discharge cutoff voltage of 0 V, and with extra ion insertion sites, exhibits more effective performance improvement on specific and reversible capacity.$^{17–21}$ However, even these methods have rapid capacity fading at high current densities, >10C, due to an increase in internal resistance and polarization losses, which directly alters the reaction kinetics of the electrochemical cell.$^{15–22}$

Here, we demonstrate a new strategy to enhance the specific capacity of LTO by developing unique nanoengineered three-dimensional (3D) frameworks. These frameworks are built by
FIG. 1. Charge and discharge curves of (a) LTO, (b) LTO/rGO, and (c) LTO/rGO/h-BN at different charging rates. The h-BN incorporated sample shows improved performance at all rates.

FIG. 2. (a) Discharge curves of c samples under different h-BN loading conditions. The optimum h-BN loading condition is 1:5 (weight). (b) Optimum h-BN loading map. (c) Cycling performance of LTO, LTO/rGO, and LTO/rGO/h-BN at 5C.

combining LTO with highly conductive reduced graphene oxide (r-GO) aerogel and hexagonal boron nitride (h-BN). This design enables efficient electron diffusion, high reversible capacity, and high electrochemical performances.
The framework is prepared by mixing LTO (>99%, Sigma Aldrich) with various weight percentages of r-GO and h-BN flakes. The r-GO/h-BN composite aerogel structure is prepared by mixing and sonicating h-BN flakes (Momentive Performance Materials, Inc.) and graphene oxide (GO) overnight at room temperature. Then, the GO in this mixture is reduced to r-GO by the previously described hydrothermal method.23–25 After r-GO/h-BN is produced, it is mixed with LTO (45:1 weight percentages) and annealed at 400 °C for 2 h.

To examine the electrochemical performance, lithium metal (Li-metal) based two electrode cells are prepared while using LiPF6 (EC:EMC:DMC = 1:1:1 in volume) as an electrolyte. The working electrodes are prepared by casting a slurry of 80 wt. % active material, 15 wt. % conductive reagent (acetylene black), and 5 wt. % polyvinylidene difluoride (PVDF) binder onto a copper (Cu) foil. Cyclic voltammetry and impedance measurements are conducted using a Biologic BSC-810 and referenced checked Gamry instrument (reference 3000).

The electrochemical behaviors, specific capacity and cycling performance, of LTO, LTO/r-GO, and LTO/r-GO/h-BN composites are extensively investigated. Figures 1(a)–1(c) shows the typical charge–discharge curves at various charge densities of LTO, LTO/rGO, and LTO/rGO/h-BN, respectively. LTO/r-GO cells have better performance than LTO cells, as suggested in the literature.13,17,18,24 However, the cells with h-BN implementation show a greater improvement in anodic stability and reversible capacities, especially at high charging rates >5C, compared with other prepared cells. However, it should be noted that the loading ratio of h-BN plays a significant role in performance. As shown in Figs. 2(a) and 2(b), at first there is a linear relationship of h-BN loading reversible capacity improvements; after a certain loading point (1:5 h-BN:GO) the cell’s electrochemical performance greatly degrades. Especially, some samples with high loading ratios, at high charging rates, are more prone to failure after a few cycles, which strongly suggests poor electron transport and loss of electrical contact. In this report, we use optimal loading ratios of 1:5, wt. %, for cell comparisons. Figure 2(c) shows long term cycling performance comparisons of LTO, LTO/r-GO, and LTO/r-GO/h-BN at a high current rate of 5C. It is very clear that h-BN incorp-orated samples have better stability and higher capacity than other samples.

Figure 3(a) shows a clear comparison of rate capabilities of LTO, LTO/r-GO, and LTO/r-GO/h-BN at 5C charging rates. The cycling stability of a LTO/r-GO/h-BN nested composite shows higher capacity and the best performance compared to other composite structures. At 20C charging rates, the capacity retention of the h-BN modified composite is almost 85%, whereas the value for others is below 75% and 55% for LTO/r-GO and LTO, respectively. When the rate returns to 1C, the specific discharge capacity of the composite also returns to a similar value, initially measured at 1C, which illustrates good reversibility. This is another indication of the importance of the h-BN addition. To understand the role of h-BN, cyclic voltammetry experiments are carried out at different scan rates [Figs. 3(b) and 3(c)]. The relationship between peak currents and scan rates shows a standard diffusion limited reaction and a faster Li+ diffusion rate for LTO/r-GO/h-BN due to its high diffusion coefficient. Moreover, extra intercalation of lithium ions (from Li7Ti5O12 to Li9Ti5O12) and surface
lithium storage reaction has been observed, which is associated with better capacity and performance due to extra and fast lithium insertion.\textsuperscript{21,26,29} The impedance spectroscopy measurements, shown in Fig. 3(c), can be further used to evaluate the electrochemical performance of r-GO/h-BN. The resistance can be broken down into three regimes: High, medium, and low frequencies, which are related to ionic conductivity, the charge transfer between electrodes, and diffusion of lithium ions in the cathode, respectively.\textsuperscript{17,18,27} Cells, without any modification, clearly exhibit higher impedance and charge transfer resistance than cells containing r-GO/h-BN. This strongly indicates that ionic diffusion is more efficient through r-GO and r-GO/h-BN modified electrodes. In the literature, it has been clearly reported that r-GO modification leads to electrical conductivity improvement and much better ohmic resistance.\textsuperscript{17,18,27} We observed a similar behavior with r-GO modified electrodes, which have a better series resistance than the r-GO/h-BN modified ones, up to 10%–50% improvement, depending on the h-BN concentration, as expected due to the insulting behavior of h-BN. However, charge transfer resistance values of r-GO modified electrodes are significantly higher than the r-GO/h-BN modified electrodes, more than two times, which clearly indicates the important role of h-BN in charge transfer behaviors due to better polarization abilities. In the literature, r-GO/BN structures are scarcely studied and improvement in the charge transfer resistance was not clearly observed;\textsuperscript{28} however, there is sufficient evidence in the literature that the single addition of h-BN results in charge transfer resistance improvement.\textsuperscript{28} The r-GO/h-BN hybrid modification clearly provides higher conductivity, better charge transfer resistance, and ionic diffusion abilities. As displayed in Fig. 3(d), the LTO/r-GO/h-BN composite also shows superior capacity and recovery rate compared to LTO/r-GO and the bare LTO. Especially, discharge capacities of LTO/r-GO/h-BN at high discharge rates of 10C and 20C are 179.5 mA h g\textsuperscript{-1} and 174.1 mA h g\textsuperscript{-1}, respectively, while those of LTO/r-GO was 161.6 mA h g\textsuperscript{-1} and 156.2 mA h g\textsuperscript{-1}, which is in line with the literature values for LTO/r-GO.\textsuperscript{17,18,27}

Subsequently, when the LTO/r-GO/h-BN mixture is incorporated into a pouch cell with a commercial NCM622 cathode, the specific capacity of this complete cell is lowered due to irreversible Li\textsuperscript{+} lost at the cathode material (Fig. 4).\textsuperscript{29–32} To overcome this degradation, these cells are modified with conductive species of Cu. We are able to increase the specific capacity of this mixture only with h-BN modified anodes up to 200 mA h g\textsuperscript{-1}. This improvement could be associated with better electron transport abilities and more stable first cycles of irreversible Li\textsuperscript{+} accumulation.

In conclusion, we have successfully developed an efficient framework to enhance the specific capacity of LTO by using an r-GO/h-BN composite structure. The cells with the h-BN modification display higher performance, in terms of specific capacity and stability. This nested nanocomposite structure allows better lithium ion diffusion, electron transport, and better lithium ion storage. It is also demonstrated that the loading ratio of h-BN is very critical to reach the optimum performance. We believe that h-BN will play a key role in achieving very high performance and a stable future for Li-ion batteries.

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The data that support the findings of this study are available from the corresponding author upon reasonable request.

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