

## The Nonaqueous Asymmetric Hybrid Technology: Materials, Electrochemical Properties and Performance in Plastic Cells

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Electric propulsion have been the cornerstone of a promised new generation of automobiles and scooter/motorcycles whose origin dates back almost a century. Although enhanced resources have been focused towards the development of this technology, the implementation of this technology seems to be in the distant future due to both technological and logistical concerns. More recently, concepts related to the hybrid electric vehicle (HEV), which contains a mixed electric / internal combustion power source has been implemented into commercial vehicles showing respectable commercial success. Between the energy storage requirements of the hybrid and that of a traditional automobile lie those of the 42V power systems of the next generation of automobiles.

Non-aqueous electrochemical double layer capacitors (supercapacitors) have demonstrated outstanding performance characteristics related to power density, safety, lifetime, and irreversible capacity (capacitance) losses upon storage. However, applications from the 42V power systems on through its electrochemically power brethren require energy storage devices of higher energy density, namely on the order of 20-30Wh/kg. Immediately, one would turn to battery technology, but in most instances this would be quite inefficient, as the required battery size would be much oversized with respect to energy so to meet the power requirements. The chemistry of battery technology such as Li-ion can be easily modified to deliver high power and considerable advancements have been made towards reported numbers on the order of 600-800W/kg. These numbers will no doubt increase with improved chemistry, however, all battery technology will suffer from one main drawback, poor robustness. This is one area where supercapacitors, because of their non-faradaic electrode reactions will excel.

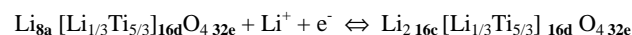
In order to increase the energy density of supercapacitors, a number of approaches have been attempted. These include the use of thick electrode supercapacitors, highly engineered activated carbons, "supercapacitors" utilizing positive and negative electrodes composed of organo-redox compounds, and asymmetric aqueous supercapacitors utilizing high capacity pseudocapacitive electrodes such as hydrated RuO<sub>2</sub> or nickel hydroxides.

### Non Aqueous Asymmetric Hybrid Technology

We have recently introduced a non-aqueous asymmetric hybrid energy storage device that maintains the robustness and upper voltage of a non-aqueous supercapacitor, yet can deliver power (>1000W/kg) at energy densities which are almost an order of magnitude greater.<sup>1,2,3</sup> The concept utilizes a nonfaradaic, capacitive (activated carbon) or pseudocapacitive (organoredox) positive electrode.<sup>4</sup> This was coupled with a non-capacitive Li intercalation compound negative electrode.

The most challenging aspect of the asymmetric hybrid cell was to identify a suitable negative electrode Li intercalation material which could match the undeniably robust performance of the non-faradaic activated carbon positive electrode material.

The spinel Li intercalation compound, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> intercalates Li at -1.5V vs. SHE (approx. 1.5V vs. Li/Li<sup>+</sup>) in a two-phase lithium intercalation reaction<sup>5</sup>



The flat two phase intercalation reaction can offset the steep, linear, non-faradaic profile of the activated carbon positive electrode of the asymmetric cell. With respect to cycle life, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> is one of the few lithium intercalation compounds that exhibit little appreciable expansion or contraction during the lithium insertion - reinsertion process.<sup>6</sup> Because of the small degree of strain, the high modulus spinel does not undergo the considerable degree of electromechanical grinding which effects the cycling stability of other intercalation compounds to a great degree. The rate capability of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> was found to be poor with respect to the demands of a high power device. Although a poor electronic conductor in the oxidized state, the rate limitation of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> was found to reside in the slow mobility of the two phase reaction boundary during the lithiation reaction. Even submicron Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> was found to exhibit inadequate charge / discharge rate capability. We have addressed and solved this blocking impediment by developing the first nanocrystalline Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> through a novel process utilizing nanocrystalline oxide TiO<sub>2</sub> precursor material. The exceptionally short Li<sup>+</sup> diffusion distances enabled exceptional capacity utilization at fast rates while maintaining exceptional cycling stability over thousands of cycles.

This paper will retrace the steps of materials selection and criteria necessary to the optimization of the asymmetric hybrid technology to this point. In addition, views and data will be presented on alternative material approaches for next generation systems. Performance of the technology implemented in small and large plastic cells will be presented in the form of Ragone plots, low, and elevated temperature performance and cycle life.

### References

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