

Recent Advances of Alternative High Power Nonaqueous Chemistries based on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Negative Electrodes

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There is a relatively wide gray area within the Ragone plot of power and energy density between batteries and non aqueous electrochemical double layer capacitors (supercapacitors) where new chemistries are in increasing demand for both stand alone and extended pulse power assist application. Five years ago at the 1999 Fall ECS Conference in Honolulu our group introduced a new cell non-aqueous asymmetric hybrid cell chemistry based on nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative electrodes combined with an activated carbon positive electrolyte and high rate electrolytes. This paper will quickly overview the development of the technology since that time and for the first time introduce new high power/energy technology which expands on the basic chemistries.

The nonaqueous asymmetric hybrid (NAH) was developed with the goal to have energy densities compared with supercapacitors while at the same time retaining the power and most importantly the notorious cycle life and robustness of a supercapacitor. In order to increase the energy density of the supercapacitor by a factor of 5-10 and maintain cycle robustness, a non-aqueous asymmetric hybrid configuration was developed¹ incorporating a capacitive or pseudocapacitive positive electrode coupled with a Li-ion insertion (intercalation) negative electrode². The insertion electrode enables the pinning of a low initial potential not attainable for a capacitive electrode thereby resulting in a significant increase of average cell voltage. This combined with a large specific capacity of the electrode results in a significant increase of energy density. Normally such a combination of dissimilar electrodes would result in poor performance, worse than what a battery and standard supercapacitor could deliver in an extrinsic hybrid arrangement. The disparity between the intercalation and non intercalation electrodes needed to be addressed. This was accomplished by engineering a negative Li insertion electrode with properties that reflect that of the capacitive positive electrode, namely rate and cycle life. The most challenging properties to overcome was the ability to maintain >100,000 cycles and the ability to accept full charge within 15 seconds. The former was addressed by utilizing one of the only intercalation materials that undergo 0% volume change upon lithiation³ a lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel material first investigated in 1982 as a potential anode for Li-ion batteries⁴. The high rate issue of the latter was resolved by the introduction of a nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ⁵. The NAH exhibited packaged specific and volumetric energy densities approximately 300-500% that of the best supercapacitors while maintaining outstanding robustness and performance at -30°C. Fig. 1 demonstrates that the cycling stability of the LTO enabled the cell to cycle >350,000 cycles with little capacity fade after 1.5yrs of continuous cycling.

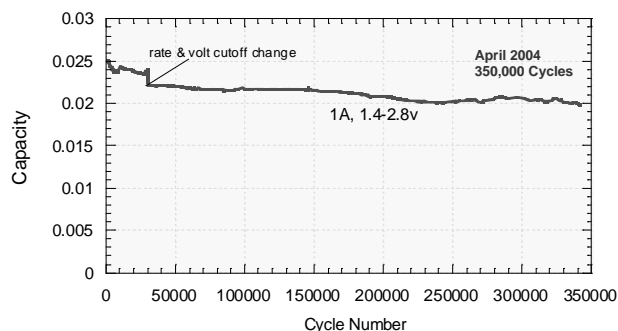


Fig. 1 Cycling stability of a plastic $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /activated carbon nonaqueous asymmetric hybrid cell cycled at 24°C from 1.4 to 2.8V at approximately 40C.

Certain applications are not as cycle life intensive where >100,000 cycles are necessary. Energy densities of the NAH may be increased through the use of organo-redox positive electrode at the expense of cycle life⁷. In order to increase the energy density/power density even further, the positive electrode can be composed of a lithium insertion material/activated carbon composite⁸. For example, a composite/nanocomposite of LiCoO_2 and activated carbon can be fabricated and applied as the positive electrode. The ratio of intercalation material and activated carbon further expands the flexibility of the energy storage cell to be tuned to a specific devices requirement. The composite packaged cell exhibits 20-35Wh/kg at 2000-3000W/kg. Although power and energy have made a considerable jump in value, the cycle life is rated for applications that require less than 3,000-5,000 full depth of discharge cycles. At this meeting we will introduce a newer technology with much improved energy densities, similar power and improved cycling stability via the introduction of new electrode materials.

References

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