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Rechargeable Batteries For The 300-mile Electric Vehicle and Beyond

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Lithium-ion batteries have been a key component in the modern portable electronic technology revolution and they are indispensable for our everyday life. Despite their huge success and ubiquitous presence, there is an ever increasing need for batteries with significantly higher energy and power densities to meet the demands of new consumer devices, electric automobiles, aerospace technologies, power tools, and various future energy hungry applications. Notably, all-electric family automobiles with a driving range of 300 miles or more on a single charge require batteries with more than twice the energy density, a step increase in cycle life and significant reduction in cost compared with today's Li-ions. It can be shown from calculations using a typical family car such as a Toyota Camry that a 300-mile range all-electric vehicle would need Li-ion cells with specific energy >500 Wh/kg as opposed to the 225 Wh/kg available today (1). In the Camry weighing about 1500 kg, the engine plus gasoline tank contributes approximately 400 kg. This is the weight available for the battery pack without altering the conveniences in the car. Assuming that a kilowatt-hour of battery will provide 3 miles of driving, a 100 kWh battery is required for driving 300-miles on a single charge. In practice, it is necessary to oversize the battery by about 40 percent for two purposes; i) to have a 20 % reserve capacity in the normal operation of the car, and ii) to compensate for the capacity fade of 20% during the life of the battery. Thus, the 300-mile car would be powered by a 140 kWh battery initially. The weight energy density of such a 400 kg battery pack then is 350 Wh/kg. If the efficiency for the conversion of cells to battery pack is 60 %, the energy density of the cells to build the 300-mile range battery pack is ~580 Wh/kg, more than two and a half times that of today's cells. In order to build such batteries using Li–ion technology, positive electrode materials having significantly higher specific capacities than those presently available are needed

The highest specific capacity Li-ion positive electrode $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$, (NCA), a variant of the original Li intercalating layered $LiCoO_2$ (2). NCA has a reversible specific capacity of about 190 milli-ampere hours per gram (mAh/g), which is in the neighborhood of 70% of the theoretical one-electron reaction of this electrode material. Commercial 18650 size Li-ion cells built with NCA and graphite negative electrode is approaching 240 Wh/kg. The reversible capacity for a transition metal oxide positive electrode material capable of one-electron reaction is ~270 mAh/gram. A 3.6 V Li-ion cell built with such an oxide cathode and a graphite negative electrode would exhibit a specific energy of about 300 Wh/kg. Presently, a class of positive electrode materials potentially capable of such high capacity is the lithium rich layered manganese oxides (layered LMO) (3). For example, $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ and other oxides related to it have shown practical reversible capacities up to 250 mAh/gram, albeit at low rates. The projected energy density of the corresponding 18650 Li-ion cells is 280 Wh/kg, increasing to approximately 320 Wh/kg if the graphite negative electrode is replaced with silicon. This evolution in the energy density of Li-ion batteries is presented in Figure 1 using the highly engineered 18650 Li-ion cells as examples. Clearly, this is still short of the 580 Wh/kg cells required for the 300-mile vehicles. On a more positive outlook all- electric-vehicles with 150-200 mile range are possible with such batteries, and they will become prevalent if they can be made cost effective. The 200 mile range cars will be powered by 90 kWh battery packs which at the best case scenario price of $400/kWh will cost $36000, too high for an average family car.

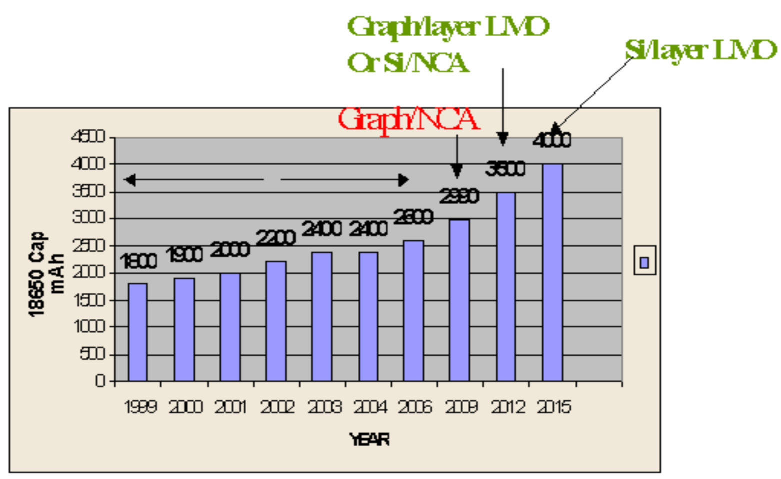

Figure 1: Figure 1: Past and projected capacity evolution of 18650 Li-ion cells. The layer LMO represents the Li-rich layered manganese oxides such as $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$. This 18650 cell with silicon anode is projected to have 4000 mAh capacity and ~ 320 Wh/kg. Their approximate volumetric energy densities may be obtained by multiplying this value by 2.5.

Long-term Prospects

The specific energy (Wh/kg) of an electrochemical couple is given by Equation 1.

Energy density (Wh/kg) =

$$\frac{\textbf{Cell Voltage (V) x 1000(g) x 26.8 Ah}}{\textbf{(kg) x Eqv.wt(g)}} \qquad \textbf{[1]}$$

where V is voltage and 26.8 Ah is the theoretical capacity of the electrochemical couple for reactions involving one equivalent weight (eqv. wt) of the reactants. Equation [1] teaches that electrochemical couples exhibiting very low equivalent weights and high voltages are needed for building super high energy density batteries (Figure 2) (4).

The equivalent weights of Li-ion batteries range from 130 (for the best case scenario with a silicon anode capable of reversibly alloying with 4 moles Li per mole of Si and a lithiated metal oxide with a specific capacity about 250 mAh/gram as discussed above) to 235 for the graphite/$LiCoO_2$ cell intercalating 0.6 moles of Li per $LiCoO_2$ to yield 140 mAh/gram capacity (5). It should be noted that Li-ion cells utilizing silicon anodes and layered LMO are far way from being practical due to many materials and cell design challenges. Clearly, advanced super high energy density battery couples should be sought and developed.

Figure 2 shows that coupling the most electropositive element Li with highly electronegative and light elements from groups VIB and VIIB of the periodic table provide the best opportunities for building super high energy density batteries. Figure 3 displays the theoretical energy densities of several such high energy density Li battery couples along with those of several well-known practical batteries and the hydrogen-oxygen (H_2-O_2) fuel cell. The Lithium-Fluorine (Li-F_2) battery couple is the highest energy density system theoretically possible but it is impractical because of the extreme chemical reactivity of F_2.

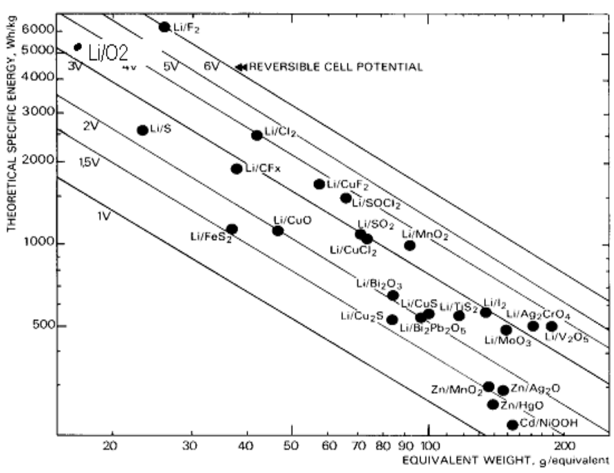

Figure 2: Figure 1: Energy density map depicting theoretical energy densities of battery couples versus equivalent weights for various cell voltages

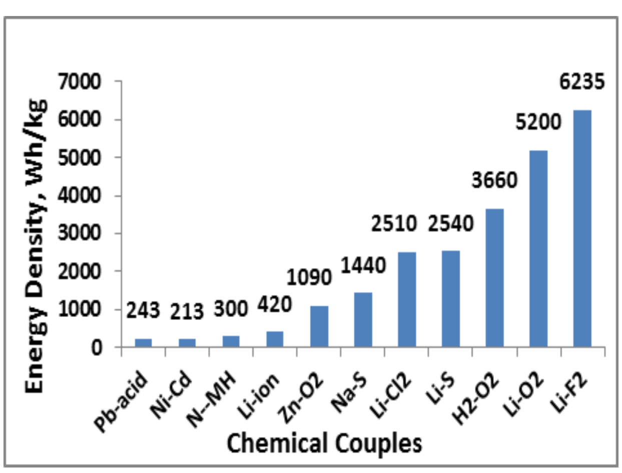

Figure 3: Theoretical Energy densities of battery chemical couples

Similarly, the Li-Cl_2 couple is a difficult system to practically implement. This leads to the lithium-oxygen (Li-O_2) couple as perhaps the most logical candidate for the ultimate high energy density battery with the Lithium-Sulfur (Li-S) system placing a distant second. In this paper I will present some recent efforts to develop a rechargeable Li/O_2 battery (6-8). The performance of the Li/O_2 battery will be compared to that of the rechargeable Li/S battery (9). A major factor limiting the cycle life of rechargeable the Li/S battery is the solubility of the lithium polysulfides in organic electrolytes, and the related sulfur shuttle reactions. An avenue to overcome this problem would be to decrease the solubility of sulfur with the use of metal sulfides as cathodes (10). Some past work I have done on such batteries is worth revisiting. Specific examples are Na/NiS, Na/CuS, Na/FeS_2 and Na/NiS_2 rechargeable batteries, and possibly their Li counterparts for the future. Interestingly, renewed interest in these batteries are beginning to emerge (11) which should be highly encouraged. Ultimately, energy from electrochemical reactions is limited due to constraints imposed by the Periodic Table of elements. Moore’s law cannot predict the evolution of high energy density batteries (4).

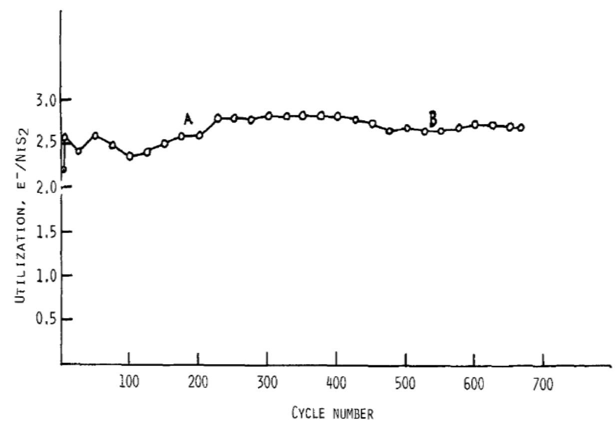

Figure 4: Cycle life data for a Na/NiS_2 cell (10)

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