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New Generation Lithium – Ion Batteries with Intermediate Bands for Stationary Energy Storage

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Abstract

A new theory on stationary energy storage is further improved by using non-linear Lithium-Ion batteries with intermediate bands. It will be therefore shown that by using the above modern chemical based technology, then the statical energy storage will be very much increased in comparison to the current technology. Hence, the energy storage will be increased to many hundreds of MW or even to GW. Beyond the above, the cost per KWh will be very much reduced. The proposed method can be also used to several other types of batteries, as well, like advanced lead-acid and lead-carbon batteries, sodium-based batteries and flow batteries.

Key Word and Phrases
New Generation Lithium-Ion Batteries, Stationary Energy Storage, Intermediate Bands, Statical Chemical Energy Storage, Lead-Acid Batteries, Lead-Carbon Batteries, Sodium-based Batteries, Flow Batteries.

1. Introduction - Details of Proposed Technology

Grid energy storage, which is also called large-scale energy storage, refers to the methods used to store electricity on a large scale within an electrical power grid. Thus, electrical energy is stored during times when production usually from power plants especially intermittent renewable electricity sources such as wind power, tidal power, solar power exceeds consumption and when additional discretionary load is turned on but consumption is still insufficient to absorb it.

The stores are used, which is referred to feeding power to the grid, at times when consumption that cannot be deferred or delayed exceeds production. In such way, electricity production need not be drastically scaled up and down to meet momentary consumption instead, transmission from the combination of generators plus storage facilities is maintained at a more constant level.

In addition, an alternate and complementary approach to achieve the same effect as grid energy storage is to use a smart grid communication infrastructure to enable demand response (DR). Both of these technologies shift energy usage and transmission of power on the grid from one time when it is not useful, to another, when it is desperately immediately needed.

Any electrical power grid must adapt energy production to energy consumption, both of which vary drastically over time. Such combination of energy storage and demand response has the following advantages:

- fuel-based power plants (like coal, oil, gas, nuclear) can be more efficiently and easily operated at constant production levels.
- electricity generated by, or with the potential to be generated by intermittent sources can be stored and used later, whereas it would otherwise have to be transmitted for sale elsewhere, or simply wasted.
- peak generating or transmission capacity can be reduced by the total potential of all storage plus deferrable loads, saving expense of this capacity.

- more stable pricing: the cost of the storage and/or demand management is included in pricing so there is less variance in power rates charged to customers or alternatively (if rates are kept stable by law) less loss to the utility from expensive on-peak wholesale power rates when peak demand must be met by imported wholesale power.
- emergency preparedness or vital needs can be met reliably even with no transmission or generation going on while non-essential needs are deferred.

Energy derived from photovoltaic and wind sources inherently varies, as the amount of electrical energy produced varies with time, day of the week, season, and random factors such as the weather. So, renewable energy present special challenges to electric utilities. While hooking up many wind sources can reduce the variability, solar is reliably not available at night, and tidal power shifts with the moon so is never reliably available on peak demand.

How much this affects any given utility varies significantly. In a summer peak utility, more solar can in general be absorbed and matched to demand. In winter peak utilities, to a lesser degree, wind correlates to heating demand and can be used to meet that demand. Depending on these factors, beyond about 20-40% of total generation, grid-connected intermittent energy sources such as photovoltaics and wind turbines tend to require investment in either grid energy storage or demand side management or both. In an electrical power grid without energy storage, energy sources that rely on energy stored within fuels (coal, oil, gas, nuclear) must be scaled up and down to match the rise and fall of energy production from intermittent energy sources.

While petroleum and gas plants can be scaled up when wind dies down quickly, coal and nuclear plants take considerable time to respond to load. Utilities with less gas or oil power generation are thus more reliant on demand management and grid storage.

The main devices with chemical basis for energy storage are the batteries. Battery storage was used in the early days of direct current electric power. Where AC grid power was not readily available, isolated lighting plants run by wind turbines or internal combustion engines provided lighting and power to small motors. The battery system could be used to run the load without starting the engine or when the wind was calm. A bank of lead-acid batteries in glass jars both supplied power to illuminate lamps, as well as to start an engine to recharge the batteries.

Battery systems connected to large solid-state converters have been used to stabilize power distribution networks. For example in Puerto Rico a system with a capacity of 20 megawatts for 15 minutes is used to stabilize the frequency of electric power produced on the island. Furthermore, a 27 megawatt 15-minute nickel-cadmium battery bank was installed at Fairbanks Alaska in 2003 to stabilize voltage at the end of a long transmission line. Many "off-the-grid" domestic systems rely on battery storage, but storing large amounts of electricity in batteries or by other electrical means has not yet been put to general use.

By the present paper a modern technology with chemical basis will be improved in order to increase significantly the storage capacity of energy for stationary applications, as well as to reduce the cost of each kWh. Hence, the Lithium-Ion batteries with intermediate bands are proposed for the chemical based stationary energy storage. The proposed method can be further used to other types of batteries, as well, like advanced lead-acid and lead-carbon batteries, sodium-based batteries and flow batteries.

Thus, the modern method which was recently used successfully by E.G.Ladopoulos [1] - [3] for the ideal solar cells with intermediate bands, will be extended by the present study to be used for the high technology Lithium-Ion batteries with intermediate bands. The behavior of such batteries will be non-linear and so they will be called non-linear Lithium-Ion batteries with intermediate bands.

By the above mentioned theory on solar energy intermediate bands were introduced within the energy gap of the semiconductor, in order to increase the efficiency of solar cells. The photons with energy less than the band gap could therefore contribute to the output device by using the intermediate band or bands, in order to jump to the conduction band. This problem was reduced to the solution of non-linear integral equations and for their solution a new and groundbreaking numerical method was proposed. Generally, in solar cells low energy photons can not excite electrons to the conduction band and then to the external circuit. Consequently, intermediate bands get advantage of the lower energy photons by allowing the electrons to be promoted to levels in the usually forbidden energy gap. Hence, through the proposed multi-step approach, then the efficiency of the solar cell is increasing. By the above mentioned research it has be shown that the maximum efficiency of an ideal solar cell containing one and two intermediate bands will be 63 % and 75 %, respectively.

Thus, the non-linear singular integral equations methods which were introduced by E.G.Ladopoulos [4] - [26] and were used successfully during the past years for the solution of several engineering problems of fluid mechanics, hydraulics, aerodynamics, solid mechanics, potential flows, petroleum engineering and structural analysis, were further extended by the above research for the solution of solar energy problems.

The proposed non-linear Lithium-Ion batteries with intermediate bands will:

- Store energy for stationary applications, with capacity in the level of many thousands of MW, or even GW, while by the current technology only a few MW can be stored.
- Have a chemical basis for energy storage.
- Safely store and release electricity.
- Are much cheaper and more efficient, than existing energy storage options, as they will have the opportunity to store several thousands of MW, or even GW.

2. New Generation Lithium-Ion Batteries with Intermediate Bands

The proposed batteries are Lithium-Ion made from LiFePO4 (Lithium Iron Phosphate) cathode and anatase TiO2 (Titanium Oxide) graphene composite anode and will be used for stationary energy storage. While with relative lower energy density than traditional Lithium-Ion batteries are used for vehicle applications, the Lithium-Ion batteries based on LiFePO4/TiO2 combination can be used for long life and low cost, along with safety and all of them are critical to the stationary applications.

Hence, of particular interests are the Lithium-Ion chemistries that are made from electrode materials of reasonable cost and excellent structural and chemical stability, as well as low heat generation, during Lithium extraction and insertion. The batteries of from LiFePO4 cathode and anatase TiO2/graphene composite anode are one kind of the requested identities.

For cathode, we are choosing LiFePO4 because of its stability, low-cost and environmental friendliness. The above material has a lower voltage of 3.45 V, than many other cathode compositions and also LiFePO4 shows flat discharge-charge curves during two-phase Li-extraction-insertion process and excellent cycling stability due to its unique ordered olivine structure. On the contrary, titanium oxide based materials including TiO2-polymorphs and Li4Ti5O12 exhibit a relative high voltage as (1–2 V), but have open structures that allow Li-insertion-extraction without much structural straining, and so it has a long cycle life. In addition, the relative high voltage vs. Li of the TiO2-base anodes helps to avoid SEI layer formation, making the battery much safer than the graphite anodes used commercially.

Thus, by the current paper we propose a non-linear Lithium-Ion battery with LiFe-PO4 cathode and anatase TiO2/graphene anode. The above proposed battery is evaluated for its electrochemical performance. To the proposed batteries is given an emphasis on long life and low cost, along with safety, for the stationary applications and so batteries of LiFePO4 cathode and anatase/graphene composite anode are characterized individually to better performance by minimizing the internal resistance and irreversible heat generation.

The Lithium-Ion batteries are the most promising stationary energy storage technology compared to other battery technologies. So, the have a big potential in stationary energy storage, as their cost continues to decrease and their safety and cycling life are improved. Such batteries are the best device for renewable integration and grid energy applications, because of their low cost, cycle life and big safety. Moreover, the use of nanomaterial in order to enable control of the electrodes at the nano-scale enable the batteries to operate at higher power.

Because of its two-phase Li extraction and insertion process, the $LiFePO_4$ compound is characterized by flat discharge / charge curves around 3.45 V. On the other hand, titanium oxides (TiO_2) are very good alternatives to graphite for battery anodes. They operate at higher voltage (1.5 to 1.8 V) than graphite and so they provide less energy than the usual Lithium-Ion batteries, but they improve very much the overall safety of the battery by avoiding solid-electrolyte interface (SIE) layer formation.

According to our proposal both anode and cathode will consist of more than one bands. By using therefore many bands than the storage capacity of the battery will increased too much. Consequently, it will be possible the construction of batteries of many thousands of MW of storage, even a storage of GW. Such a battery in shown in Figure 1.

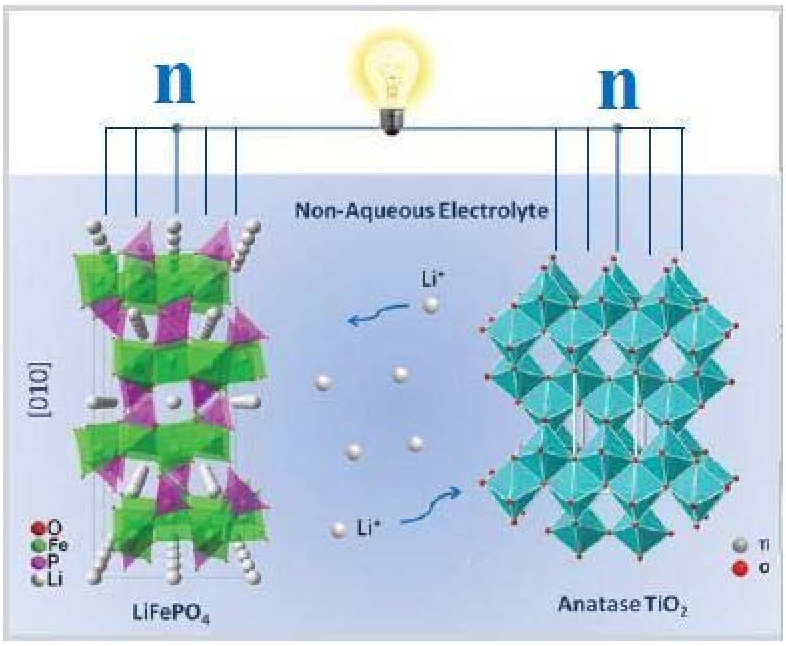

Fig. 1 A Lithium-Ion Battery with Intermediate Bands

3. Cathode of New Generation Lithium-Ion Batteries with Intermediate Bands

LiCoO2 was the first choice to work as cathode materials when Lithium-Ion batteries came out in 1990. Thus, its long history supports LiCoO2 a big progress. During that process, other cathode materials were further discovered, like LiNiO2, LiMn2O4, LiNi1/3Co1/3Mn1/3O2, LiFePO4, etc. The iron-based compounds look attractive as Fe is abundant, inexpensive, and less toxic than Co, Ni, or Mn. The phosphoolivine LiFePO4 is currently under extensive studies due to its low cost, low toxicity, high thermal stability and high specific capacity of 170mAhg−1. Reduced reactivity with electrolytes results in the very flat potentials during charge-discharge processes.

Very big advantages of LiFePO4 are :
(1) The structure of material hardly changes while Li ion intercalation and deintercalation.
(2) It holds a long voltage platform.

LiFePO4 owns an ordered olivine structure, orthorhombic space group Pnma. Its crystal constants of a, b and c are 1.033, 0.601 and 0.4693μm respectively. The framework of LiFePO4 consists of FeO6-octahedra and PO4-tetrahedra. So, FeO6-octahedra and PO4-tetrahedra contact each other by sharing oxygen vertices in b-c plane. The FeO6-octahedra then links another PO4-tetrahedra by sharing a edge. All the PO4-tetrahedra don't touch each other. Lithium atoms are situated in the interstitial voids of the framework, forming infinite chains along the c-axis in an alternate a-c plane. Li atoms occupy M1 site and Fe M2 site. The Fe atoms occupy zigzag chains of corner-shared octahedral running parallel to the c-axis in the other ac planes. O arranges in terms of hexagonal close packed structure with a slight distortion.

Hence, the proposed cathode of the "innovative" Li-Ion battery will include many bands of LiFePO4. With such an action the storage capacity of the battery will increased too much and will be in the level of many thousands of MW, or even GW. Moreover, the cost per produced KWh will be reduced too much.

The reaction of the LiFePO4 is as following. Lithium ions extract from anode to insert in cathode in the discharge process. The route is inversed as charge takes place. FePO4 is the second phase that is present on electrochemical extraction of lithium from LiFePO4. The extraction of lithium from LiFePO4 to charge the cathode may be written as (3.1) and the insertion of lithium into FePO4 on discharge as (3.2):

$$LiFePO_4 - xLi^+ - xe^- \rightarrow xFePO_4 + (1-x)LiFePO_4 \tag{3.1}$$

$$FePO_4 + xLi + xe^- \rightarrow xLiFePO_4 + (1-x)FePO_4 \tag{3.2}$$

By using *n* bands in the cathode then eqs (3.1) and (3.2) take the form:

$$nLiFePO_4 - n\,xLi^+ - n\,xe^- \rightarrow nxFePO_4 + n(1-x)LiFePO_4 \tag{3.3}$$

$$nFePO_4 + nxLi + n\,xe^- \rightarrow nxLiFePO_4 + n(1-x)FePO_4 \tag{3.4}$$

Despite the previous mentioned advantages, the observed electrochemical performances of LiFePO4 are found to be less impressive at high rates as this material has intrinsically poor ionic and electronic conductivity. Moreover, the behavior of the cathode will be non-linear.

4. Anode of New Generation Lithium-Ion Batteries with Intermediate Bands

Since the commercialization of the Lithium-Ion Battery in the 90's, the graphite has been the basic choice of the anode solid and so no other materials, like Si and Sn have yet been widely used. On the contrary, stationary energy storage systems have less stringent weight and space requirements. Hence, titanium oxide (TiO2) based anodes are a very good choice for such applications.

In addition, in battery applications, titanium oxide is much safer than graphite. Among various TIO2 polymorphs, for the anode was chosen the TiO2 because of the flat potential characteristics.

Titanium dioxide occurs in nature as well-known minerals rutile, anatase and brookite, and additionally as two high pressure forms, a monoclinic baddeleyite-like form and an orthorhombic α-PbO2-like form. It is mainly sourced from ilmenite ore. This is the most widespread form of titanium dioxide-bearing ore around the world. Rutile is the next most abundant and contains around 98% titanium dioxide in the ore. The metastable anatase and brookite phases convert irreversibly to the equilibrium rutile phase upon heating above temperatures in the range 600°-800 °C.

Thus, the proposed anode of the “innovative” Li-Ion battery will include many bands of TiO2. By this way the storage capacity of the battery will increased too much and will be in the level of many thousands of MW, or even GW. Besides, the cost per produced KWh will be reduced too much.

The reaction of the TiO2 is as following:

$$TiO_2^+ + 2H^+ + e^- \to TiO^{2+} + H_2O \qquad (4.1)$$

By using *n* bands in the anode then eqn (1.4.1) takes finally the form:

$$nTiO_2^+ + 2nH^+ + ne^- \to nTiO^{2+} + nH_2O \qquad (4.2)$$

Thus, Lithium-Ion batteries with intermediate bands are the best solution for the stationary energy storage because of their high electrochemical potential, light weight, flexibility and superior energy density.

5. Conclusions

By the current research the New Generation Lithium-Ion battery with intermediate bands has been proposed for the chemical based statical energy storage. It has been therefore shown that by using the above new chemical technology then the statical energy storage will be very much increased in comparison to the current technology. Thus, the energy storage will be increased to many hundreds of MW or even to GW. Also, the cost per KWh will be very much reduced.

For stationary energy applications cost and safety are the most important factors. Besides, the cost analysis is based on the cost per cycle. Thus, extended life guarantees lower overall cost. Moreover, properly thermal management of a battery can improve the cycling life thereby making it cost effective and at the same time make the battery safer.

In addition, thermal management very much depends on the power density requirement for various applications, sinve high operation leads to bigger polarization and resistance which causes increased thermal energy which needs to be dissipated efficiently in order to prevent thermal runaway.

Besides, some electrochemical relations have been presented as an attempt to determine the properties of the non-linear Li-Ion battery with intermediate bands. Thus, the study of the high technology batteries is very important for stationary energy storage.

Hence, among various electrode materials, the Lithium_Ion batteries using LiFePo4 cathodes and anatase TiO2 anodes are among the most promising electrode combination for stationary energy application that will provide cheap, safe and stable cycling performance.

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