

Review Paper on Battery Material and Sorting Criteria

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Abstract— The battery arcade is suffering rapid development owed to the vital request on behalf of moveable devices, electric vehicles and energy storage systems, convoying the current energy transition. Further than Li-ion batteries are of high importance to keep an eye on these multiple-speed changes and familiarize to the specificity of every use. This review-study will address some of the related post-Li ion problems and battery technologies, containing Na-ion batteries, Mg batteries, Ca-ion batteries, Zn-ion batteries, Al-ion batteries. MH-based series are also existing with highpoint on NiMH batteries, and innovative MH-accommodated Li-ion batteries. In conclusion, to simplify additional research and development certain future research tendencies and guidelines are discussed based on judgment of the different battery classifications with respect to Li-ion battery assumptions. Curiously, aqueous systems stay most possible to be given review for intensive, cost-effective and innocent manufacture of batteries; for instance to be utilized in stationary energy storage applications. Lithium-ion battery regularity has amazing inspiration on the stability and protection of the battery pack. It is consequently important to gather batteries with worthy reliability in a pack. This paper advises a new equality sorting method based on some internal benchmarks.

Keywords: electric vehicles, energy storage, stability and protection, battery technology

I. INTRODUCTION

Lithium-ion batteries are protection dangerous apparatuses in up-to-date manufacturing systems to offer control for organization purposes, such as facility, control, and communication. They are broadly used in electric vehicles and lattice storing for their high occupied voltage, high power and energy density, low self-discharge rate, and no memory effect. Due to the voltage and current limitations, a single battery cell is incapable to meet the power and energy necessities in most requests and, so, battery cells need to be connected in series and/or parallel to form battery packs. However, because of the imperfection of developed and the irregularity of working situations the actual voltage and state of charge of cells in the same pack may oscillate from each other strictly. Such variation of cells will damage the strength and security of the pack.

Lithium ion batteries generally use a graphite anode and a cathode made of lithium metal oxide generally comprised of lithium ion phosphate, lithium nickel manganese oxide, lithium nickel cobalt aluminum oxide. First generation lithium ion batteries mainly used in portable electrode used lithium cobalt oxide.

Aimed at this intention, these peripheral characteristics cannot promise the regularity of core physical properties and their development inclinations. As an effect, the regularity of a pack based on these external

characteristics may deteriorate dramatically along with aging even though the batteries within the pack have good reliability conferring to outward organization benchmarks. Through these growths external features used in the present approaches are the total considerations of various aging mechanisms inside lithium ion batteries. For instance, internal resistance is the sum of ohmic resistance of solid phase, electrolyte phase, separator, and contact resistance of collecting; terminal voltage is composed of open circuit voltage and over voltages; capacity loss includes the loss of lithium ions and the loss of active materials.

Electrochemical energy storing methods and technologies are in nonstop growth in arrears to the universal claim to speechless the current energy issues and satisfy the daily needs in which rechargeable batteries play a key role. Sodium-ion batteries and potassium-ion batteries are the most evident alternatives to LIBs since these technologies are using relatively abundant and cheap sodium elements and they have similar chemical properties to lithium, though they have been pointed out regarding their low energy density, and use of highly toxic and flammable electrolytes, as well as having rather high operating costs at their early stage of development. The sodium-ion battery is a complex cell when in operation compared to LIBs. Such batteries need to be explored and studied in the aim to establish alternative battery chemistries with low-cost, high safety and long cycle life. Here, we will review the recent battery developments beyond classical LIBs, taking in consideration electrode materials and electrolytes for cationic shuttles (Na, Mg, Ca, Zn and Al), as well as anionic shuttles such as halides. Also, we will debate the scientific challenges of the most relevant battery technologies, and how this will affect our perception of future batteries permitting to the specificity of the application. Finally, we will summarize the outcome of this review work in the conclusion part and provide new views for likely battery investigation guidelines.

II. MOTIVATION AND EXISTING GROWTH

By means of relating to LIB, sodium-ion battery takes similar chemistry for the duration of the insertion it is believed that concept, industrial and end-products commercialization developments can be adapted to the existing ones for Li-ion technology. On the first plan, Na-ion batteries are presented as alternative to Li-ion technology owing to cost-efficiency, safety and long-term sustainability. The abundance of Na compared to Li makes the cost factor decisive for choose between two technologies. In addition, Al current collector can be used with Na instead of Cu with higher costs, and no alloying between AlNa takes place. Na-ion batteries are considered safer with less thermal runaway.

However, the Na-ion battery system counts a few drawbacks which hinder its quick development as

alternative to Li-ion battery. Due to the higher atomic size and larger specific weight of Na, the theoretical capacities of the metal and of the electrode materials are lower, as well as the corresponding energy densities. The anode consists usually of hard carbon, as the graphite cannot allow the intercalation of Na ions between the carbon layers. The most common electrolytes allowing transport of Na ions are based on either carbonate-based solvents or ionic liquids. A large number of potential cathode materials have been explored in the last years, consisting of structurally stable polyanionic materials and layered transition metal oxides providing high energy density and high operating voltages.

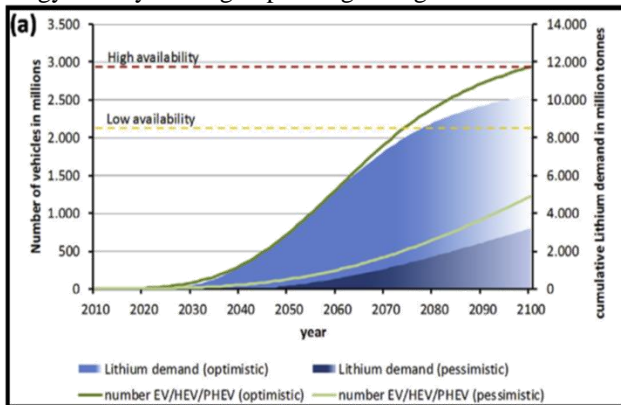


Fig. 1: Long-term assessment of lithium availability and demand, and number of electric vehicles over time.

III. CATHODE MATERIAL

Metal oxide cathode materials are the most developed and promising cathodes employed in SIBs. Similar to LIBs, the Na_xCoO_2 has been studied already in the early 1980s. This cathode demonstrates reversible intercalation of Na^+ ions in the phase Na_xCoO_2 ($0.5 < x < 1$), accompanied by a phase transition of the layered structure involving a change from octahedral or trigonal prismatic coordination to the monoclinic ally distorted phase packing. Similarly to Na_xCoO_2 , Na_xMnO_2 polymorphs are widely investigated as cathode materials for SIBs. The a- Na_xMnO_2 phase is structurally more stable than its homologue high-T orthorhombic b- Na_xMnO_2 phase (Fig.2a), and shows a layered structure with monoclinic distortion. Based on an initio studies, it has been found that the structure shown in (Fig.2b) for $\text{Na}_{0.44}\text{MnO}_2$ have the lowest energy in the S-shaped tunnel. The intercalation of Na^+ in the a-phase allows $185\text{mAh}\cdot\text{g}^{-1}$ at C/10 rate with 71% capacity retention over 20 cycles, meanwhile 70% after 100 cycles is delivered when comparing to b-phase. The charge/discharge profiles shown in (Fig.2c) indicate a multi-step processes in relation to the presence of intermediate phases' transformations. It seems that not all these transformations and reaction paths are well understood and consequently not yet determined in details.

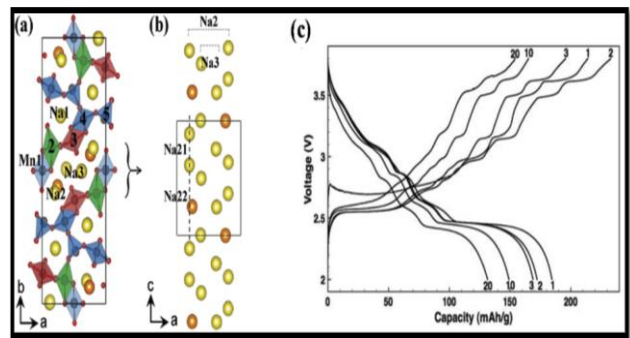


Fig. 2: a) Crystal structure of $\text{Na}_{0.44}\text{MnO}_2$ with five crystallographic sites for manganese and three sites for sodium ions. b) Most probable sodium configuration is in the shaped tunnel along the c-axis where the Na_2 site has two different sodium positions. c) Voltage profile of NaMnO_2 after multiple cycles at C/10.

Further to the oxides, a series of sulfate, phosphate and fluoride materials has been studied as cathodes for SIBs. Na-S batteries undergo the same challenges as Li's batteries regarding polysulfide dissolution and dendrite formation, which will not be approached in this review work. In this category of material cathodes, $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ showed the most interesting electrochemical features with a voltage of 3.8 V and delivering a capacity of $100\text{mAh}\cdot\text{g}^{-1}$ and 50% capacity retention at high rate 20C. The crystallography of this system is under study, where Na seems to occupy three different specific sites.

IV. ANODE MATERIAL

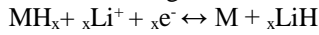
Graphite anodes commonly used in LIBs, are not suitable for the intercalation of Na^+ ions with larger ionic radii. Hard carbon was demonstrated as a host to accommodate inserted Na^+ ions. Furthermore, similar to lithium, pure metals, alloys, hydrides and oxides have been studied as different alternative known mechanisms operating in addition to intercalation, such as alloying and conversion reactions.

Demonstrated a half-cell battery with hard carbon having $200\text{mAh}\cdot\text{g}^{-1}$ capacities, with a decent rate capability over 180 cycles when using the same electrolyte. At present, hard carbon is selected to be the most suitable anode for SIBs, although a wide series of carbonaceous materials with different shapes and nanostructures are under study as well. The first tests with hard carbon anodes led to an initial capacity of $220\text{mAh}\cdot\text{g}^{-1}$ in NaClO_4 electrolyte, which decreases during cycling. Hard carbon C1600 was reported as anode of Na-ion battery. These electrodes were tested in different electrolyte media. Capacity retention was 90% over 50 cycles where an initial capacity $413\text{mAh}\cdot\text{g}^{-1}$ is obtained in the presence of 1 M NaClO_4 .

V. LITHIUM-ION BATTERIES ACCOMMODATION METAL AS ANODES AND ELECTROLYTE

Beside aqueous alkaline systems, LIBs are also developed with the aim of increasing the energy density of the electrodes. Most of the current anodes use Li intercalation into carbonaceous materials, mainly graphite. Though efficient in terms of cycle life (with formation of a stable SEI) and kinetics, these materials are intrinsically limited in capacities (typically $370\text{mAh}\cdot\text{g}^{-1}$ for graphite). To improve

the energy density, other reactions are foreseen like alloying with highly capacitive elements (Si, Sn) or conversion reactions. Aimed at the latter metallic hydrides have shown over the past decade that they offer an interesting alternative to other material. The following conversion reaction:



Using metal hydrides brings several advantages: low potential for anodes, low polarization and very high capacities. This latter parameter depends on both the molar mass M. Again, Mg-based hydrides have been studied due to the light weight of Mg, its abundance and low cost. From the early works, it was observed that the reaction is thermodynamically favorable but kinetically sluggish. This can be overcome by a cautious Nano structuring of MgH₂ and by tuning the composition of the composite electrode handle the poor electronic conductivity of the hydride and large volume changes (84%) upon process. Despite these efforts, even if the lithiation is straightforward, delithiation remains very challenging at room temperature for this hydride. For a better understanding of the limiting factors, the reaction was studied in 2D geometry using a 1 mm thick MgH₂ thin film. This model system showed that the lithiation is indeed fully completed at the first cycle with a doubling of the film thickness, while only 25% of de-process could be achieved. From TEM images it was shown that the cohesion of the film was preserved. Resistivity measurements indicate that the formation of metallic Mg increased the conductivity of the film. Therefore, the poor de-process rate of the film was assigned to the kinetic limitations related to poor mass transport at room temperature.

To overcome this drawback, formulation of composite materials can be valuable. As an example, mixing different amounts of MgH₂ and TiH₂ brings new insights into the reaction mechanism.

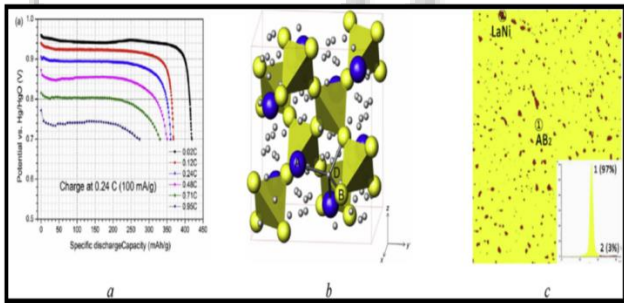


Fig. 3: a) Discharge performance of the C15 type Ti_{0.2}Zr_{0.8}La_{0.03}Ni_{1.2}Mn_{0.7}V_{0.12}Fe_{0.12} alloy showing maximum discharge capacity of 420mAh g⁻¹. b) Crystal structure of deuteride of the C15 alloy studied by neutron powder diffraction with H/D atoms. c) Presence of a secondary LaNi intermetallic (3%) catalyzing hydrogenation of the main Laves type intermetallic.

Overall, to discard any issue with liquid electrolytes during voltage solicitation, the use of solid-state electrolytes based on LiBH₄ have been investigated at high temperatures with significant improvements of the reversibility and cycling performance of the hydride anodes. A detailed review has been published recently on the contribution of hydrides to solid-state batteries. The study highlights the possibility of next generation LIBs with high

capacity and energy density where safer solid-state electrolyte is used instead of a carbonate-based liquid one.

VI. COMMONLY USED CRITERIA FOR UNIFORMITY SORTING

Seven commonly used external sorting criteria, i.e., capacity, internal resistance, discharge curve area, ratio of the capacity of constant current charging stage to the capacity of constant voltage charging stage (capacity ratio), platform efficiency, median voltage, and plateau voltage of incremental capacity (IC) curve.

A. Capacity Q_{all}

As a LIB uniformity sorting criterion, the full capacity of the battery Q_{all} directly reflects the continuous power supply capability and is one of the most important characteristics of LIBs. Usually, Q_{all} is determined by taking the average of charge and discharge capacity at 1C rate.

B. Internal Resistance Rohm

The internal resistance describes the difficulties in the movement of electrons and ions inside the battery. In this work, Rohm at 50% of SOC is measured by using a resistance tester.

C. Area of Discharge Voltage Curve, S_{DISC}

The discharge voltage curve contains information of discharge platform, discharge cut-off point, internal resistance, and capacity. The area of the projection under discharge voltage vs. time curve at 1C, S_{dis}, is calculated as:

$$S_{disc} = \int U dt$$

D. Ratio Of The Capacity Of Constant Current Charge Stage To The Capacity Of Constant Voltage Charge Stage, Q_{C/V}

In a 1C constant current and constant voltage charge process, let Q_c denotes the capacity in the constant current stage and Q_v denotes the capacity in the constant voltage stage. The capacity ratio Q_{c/v} is given as:

$$Q_{c/v} = Q_c / Q_v$$

E. Platform Efficiency, H_{PE}

The platform voltage of the LiCoO₂ LIBs under the test in this research is 3.6 V. The partial discharge capacity Q_{3.6} denotes the actual usable capacity when a fully charged LIB (terminal voltage is 4.2 V) is discharged to 3.6 V at 1C rate. Then the platform efficiency is defined as:

$$\eta_{pe} = (Q_{3.6} \div Q_{all}) \times 100\%$$

F. Median Voltage, U_{MD}

The median voltage U_{md} is the battery voltage at 50% of SOC when the battery is discharged at 1C rate.

G. Plateau Voltage of IC Curve, U_{IC}

IC curve is the profile of dQ/dU vs. terminal voltage U in constant current charge or discharge process. Each peak of IC curve demonstrates the capacity charged/discharged corresponding to a certain voltage plateau. It is demonstrated that the voltage values of plateaus shift with battery degradation and can be used as a health index of LIBs. The voltage of the maximum peak of a discharging IC profile, denoted as U_{IC}, is selected as an external criterion candidate.

VII. PRELIMINARY SCREENING ACCORDING TO EXTRACTION RELIABILITY

To guarantee the extraction reliability of each external criterion, the variation coefficient c_v is employed to give a preliminary screening of the seven external criterion candidates. It is defined as:

$$C_v = \frac{\sigma}{\mu}$$

Where σ and μ are standard deviation and mean value, respectively

The batteries with different materials or shapes may have different parameter sensitivity and correlation between parameters and degradation. This paper only proposed a common approach for extracting LIB sorting criterion. The ohmic polarization and the reaction polarization within the battery become more and more serious with the aging of the battery. On one hand, the increase of ohmic and reaction over potentials leads to decrease of time duration to reach the charge cutoff voltage and decrease of charged capacity in the constant current stage. This is the reason that the capacity ratio Q_c/v decreases with cycle number.

The comparison shows that including internal criteria in battery uniformity sorting can significantly prolong the battery pack life. The battery pack RS assembled from random selected cells has the shortest cycle life. Compared with pack EC using only external criteria packs IC and IC+EC extend the pack life by 53% and 79%, respectively. The comparison of packs IC and IC+EC shows that external criteria and internal criteria are complementary to each other in extending the life of battery packs.

VIII. ECONOMIC ASSESSMENT

Based on the operating revenues earned so far and the predicted lifetime of the batteries, total expected revenues were estimated for the Time of Use tariff, the promotional plan, and the combination of the Time of Use pricing and the discount incentive. It is also estimated how much revenues per kWh capacity are expected from the two batteries during the predicted lifetime to discuss the economics of the Li-poly and Sealed Lead Acid battery systems. The evaluation process is as below.

- 1) Find expected revenues per discharged kWh energy from actual earnings and discharged energy during the field operation. Note that revenues in the first year of the field operation were not counted in this calculation because the battery systems were at stabilization stage in the year of 2014 when occasional fixes and adjustments were made on the system hardware and operating software. Also only incentive plan II was considered for the calculation, since the plan I was transitional.
- 2) Calculate from the capacity fading curves total discharge energy available over the remaining cycles to the end of battery lifetime. The capacity degrading curves indicates how many cycles are available to the end of service life. Total amount of available discharge energy is calculated by multiplying the operating Depth of Discharge of battery by the area between the present

cycle and the ending life cycle under a capacity degrading curve with the respect of cycle.

- 3) Add the expected revenues for remaining cycles of the actual revenues earned so far to find total expected revenues during entire lifecycles of the batteries.

If the battery systems are assumed to operate throughout the entire lifetime under the combination of the TOU tariff and incentive plan situations can dramatically improve. Since the length of operation period that benefits from the generous incentive plan extends much longer, the incentive revenue per kWh capacity rises to \$681 for the Li-poly battery and \$533 for the SLA battery, leading to totals of \$933 and \$625 for the Li-poly and SLA batteries, respectively.

IX. CONCLUSION

Longer cycle lifecycle and enhanced cell-to-cell reliability of packs are realized by mixing constraints of an easy electrochemical model to the arranging benchmarks. The projected EM model constraint identification and uniformity sorting method are easy-to implement in the formation process before new batteries are carried. It can also be used to suggestion the internal features of batteries in the controllers of battery management systems or battery chargers. With any further equipment venture, the future process can support the pack performance pointedly.

However, in order to improve the performance of the lead acid battery and reduce its cost, it is not enough to replace lead dioxide electrode with air electrode merely. Future studies need to be carried out in order to:

- 1) Develop cell structure design to obtain a thinner Pb electrode and a greater geometric area of two electrodes.
- 2) Establish a new negative electrode reaction system with a higher active material utilization rate.
- 3) Look for new catalysts to replace platinum in air electrodes to reduce the high cost of these electrodes.
- 4) Build and test lead air battery electrodes to validate models.

There is no shortage of lithium (the mineral raw material), but there is shortage if highly pure lithium carbonate and lithium hydroxide (the chemical) as lately shown, for example, by the scarcity of battery grade lithium lately recorded by the Germany's company willing to start large scale electric bus manufacturing. In brief, the reuse and the recycling of LIBs is no longer an option but an inevitable need for both batteries for EV manufacturing.

Energy storage in lithium-ion battery is essential to expand the uptake of clean and renewable electricity for all energy need including and foremost for powering electric vehicle.

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