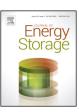
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The performance of Pb-acid cells linked to supercapacitors under partial state of capacity cycling conditions



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ABSTRACT

A comparative study was done based on the charge acceptance of small valve regulated Pb-acid cells at different states of charge (SoC) with a parallel configuration of supercapacitors at 1.4, 5.0, 10.0, 21.4 and 31.4 F/A h ratios. The study found that a hybrid system of a Pb-acid cell that was charged at a constant voltage with a relatively small supercapacitor configuration resulted in a significant improvement in both the peak current as well as the charge acceptance current over a 5-s period. The cell configuration at 20% SoC with a 31.4 F/A h capacitor showed the largest improvement, where a charge acceptance current of 16 times in magnitude was observed in comparison to a cell with no supercapacitor. A 12V battery was assembled with cells at different SoC where each cell was linked to a supercapacitor in parallel. The battery showed that there was a significant improvement in its partial state of capacity cycle (PSoCC) ability with a 5 times increase in the number of achievable cycles for the first cycle unit when compared to a similar battery with no supercapacitor. There was also an improvement in maintaining the C20 capacity that followed each PSoCC test unit. By monitoring the individual cell voltages, the main cause of failure was the 'weakest link' cell at the lowest SoC that was significantly over-charged during the PSoCC sequence and subsequently over-discharged during the C20 capacity tests. A significant improvement in the charge acceptance and cycle-ability of a Pb-acid battery can be achieved by a simple parallel configuration with modern supercapacitors.

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1. Introduction

There are many new advancements to improve the performances of energy storage devices with a fair amount of focus on the Pb-acid battery to accommodate the new demands of modern internal combustion engines (ICE) vehicles and the use of the Li-ion batteries in the portable electronic market and electric vehicles (EV). The challenges in the performance requirements of a battery in various fields of application can be broadly summarised as [1–3]:

 The capacity or power per mass of the battery needs to improve and, unrealistically or not, their utilisation are often compared to other energy systems, such as the ICE use of petroleum fuel or hydro-electric power of water storage dam systems. In simple

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terms, how much energy can be produced from the size and weight of a battery?

- With the increase in the need for portable power requirements, the rate of discharge and the recharge ability of the battery have become important. How fast can the battery be discharged and charged and utilise its energy as efficiently as possible?
- The ability of the battery to capacity cycle effectively when subject to diverse applications has to be optimised in terms of the expected life of the battery versus the depth of discharge. How long can the battery be used in a range of applications, where the challenge is often to convert the number of capacity cycles at a certain depth of discharge reported by the supplier to calendar years in application?
- With the increase in the usage, power and size of the battery, the safety aspects and the ruggedness of the battery when exposed to a range of harsh conditions in both abuse and non-abuse scenarios have become key factors in commercialising energy storage systems. How big is the effect on the user's health and the environment if the battery is subjected to a hazardous situation such as a vehicle accident or when some limit condition in charging or discharging is exceeded?

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These are but a few of the demands that are placed on a battery, which also has to be supplied at the lowest possible comparative price. These points can create opportunities for both the researcher and manufacturer to configure the battery within an application in terms of its availability, durability and cost-effectiveness. This is done not only by improving the internal chemistry of the battery but also by considering and managing it in an optimised system for a particular application.

History has shown that energy storage devices and their related chemistries that are able to adapt quickly to provide solutions when new applications and technologies emerge tend to survive the rapidity of industrialisation and technology development [4,5]. In designing batteries, there is often not a 'one-size-fit-all' approach, where one type of energy storage system is able to fulfil all the requirements for all possible types of applications. By understanding the specific energy requirements of an application, a combination of energy storage systems can be considered where the specific capabilities of such systems are then optimised in terms of their life expectancy, cost, weight and/or size within a specific application. In general, electrochemical batteries are defined as devices that have a comparatively high energy density with lower specific power density when compared to supercapacitors [4]. The life of a battery would be limited by a number of factors, such as the depth of discharge during cycling, the temperature conditions in application and the rate of recharging. This can range from a typical modern vehicle battery with a lifespan of 3-5 years to a battery used in stand-by power with a lifespan of 8–10 years. On the other hand, capacitors or modern supercapacitors can be seen as storing static electrical energy, and they are considered to be more robust when compared to batteries in terms of cycle life and produce significantly higher peak power over shorter periods of time with limited energy density [6]. A hybrid energy system would consider the advantage of the high power capabilities of supercapacitors with the suitability of a high volumetric energy density of a battery [11].

Over the years, the robustness of the Pb-acid battery has shown to adapt in its internal and external design to a diverse range of applications and it can transition relatively quickly to provide energy solutions for new emerging technologies. This can be seen in the transition from a simple starting lighting and ignition (SLI) battery from the beginning of the 20th century, which required the user to maintain the battery regularly by replenishing it with water to a sealed, maintenance-free or limited maintenance battery, such as described as absorptive glass mat (AGM) or valve-regulated lead-acid (VRLA) and more recently, the enhanced flooded battery (EFB) [1]. The modern demands and changes in technology often require these batteries to work at partial state of charge cycling (PSoCC) conditions, and in physical spaces that often do not allow for the emission of corrosive or explosive gases [1]. When compared to other competing energy storage technologies, the Pb-acid battery design has also been able to adapt its use to large industrial stand-by and vehicle traction batteries in fork-lifts or mining vehicles. In addition, because of its maturity, the Pb-acid battery has developed a good recycling infrastructure globally, which decreases its manufacturing costs and accessibility of raw materials with an expected longer capacity life-cycle [7,8].

With the increase in faster computing power and power electronics, BMS has been developed to manage the battery interface carefully within its application in order to optimise the power usage and maximise the cycle life [1,3]. Within the use of the Pb-acid battery, the BMS can be relatively simple allowing for the occasional over-discharge or over-charge to occur in the application without excessive long-term damage to the functionality of the internal chemistry. This is accompanied by the ability to combine some diverse energy technologies with an optimised systems approach where the use of batteries with supercapacitor

banks within vehicles has been studied and demonstrated extensively [9]. Hybrid energy storage systems (HESS) can be defined as hybrid systems that are either passive while supercapacitors are paralleled with cells or batteries to provide the energy where the restriction of the management of power flow is then limited [10,11]. A more active HESS approach would be to have power electronic converters that allow for individual management of the supercapacitor supply and battery management, which in turn becomes more expensive. For both types of approaches, the challenge will be to manage the utilisation of the energy in an ageing system, where the electrochemical battery would often age at different rates under different applications when compared to the use of supercapacitors, where the difficultly would be to predict and design suitable models within the lifetime management of the energy unit. On the other hand, Pb-acid batteries, such as the UltraBattery®, have emerged by combining the capacitor type chemistry with electrochemical storage within the cell assembly itself [12].

The challenge in large battery pack configurations is the assembly of cells in series to achieve higher voltages. For typical Pb-acid SLI batteries, there are six cells in series to achieve 12 V. With the increase in power demand of electric motor drives and power electronics, the requirements can be up to 36 V and 48 V systems. Batteries of up to 400 V are assembled for an EV that would typically have cell modules of more than 100 to 120 in series. The complexity of cell balancing and careful BMS control becomes one of the most challenging and demanding development requirements [9,11].

The unbalanced cell voltage or state of charge with a battery of any size will limit the life expectancy of the entire battery while excessive strain will be placed on the rest of the cells in the pack [13,14]. The unbalanced effect is usually not evident in a new battery pack where each cell in series should deliver the same capacity within certain tolerances. These tolerances become important when a battery is subjected to variable current rates and excessive capacity cycling at various states of recharge and/or within deep discharge applications to the prescribed lower voltage limits. In particular, subjecting the battery to a PSoCC, where the influence of the weaker cell would place strain on the rest of the cells and accelerate the decrease of the expected life-cycle performance of the entire pack. The subsequent failure of the full battery pack would be due to the imminent failures of the weakest cell. This problem can be alleviated in some way by introducing elaborate cell balancing protocols or as shown in this study, by introducing a parallel configuration of the cell with a supercapacitor [14,15].

This study also considered the influence on the charge acceptance of the system by using different sized supercapacitors (F) with a Pb-acid cell (Ah) ratio where the cell would be at different SoC. The study also looked at the effected of an unbalanced set of cells within a battery that was subjected to a PSoCC test, and the benefit of having a set of supercapacitors paralleled to each cell over the expected life of the battery in an accelerated life cycle test.

2. Experimental

The influence on the charge acceptance of a 7 A h VRLA Pb-acid cell connected to supercapacitors in parallel of different sizes was determined by using electric double-layer supercapacitors with an operating voltage of around 2.5 V. They were rated at 10 F, 35 F, 70 F, 150 F and 220 F and would give a capacitor (F) to battery cell capacity (A h) ratio of 1.4, 5.0, 10.0, 21.4 and 31.4 (F/A h) respectively and their specifications are summarized in Table 1. Their respective gravimetric energy density and power density are also shown and compared to the values of the Pb-acid cell used in this study. Vision

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