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Assessment of lithium-ion capacitor for using in battery electric vehicle and hybrid electric vehicle applications

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ABSTRACT

This paper represents a novel lithium-ion capacitor model. The proposed model has significantly high accuracy (less 4%). The model is an extension of Zubieta model for EDLCs. The proposed model consists of three capacitors, representing the influence of temperature, current rate (ΔC_1) and SoC (ΔC_2) on the capacitance of LiCaps, respectively. Unlike to the electrical double-layer capacitors, the model contains two resistances, illustrating the charge and discharge processes. Then, a self-discharge resistance is added to demonstrate the long term effect on the LiCaps capabilities. This model is able to predict the lithium-ion behavior during constant charging and discharging as well as during short pulses duration.

The parameters of the model have been derived based on the extended characterization tests that have been carried out.

The investigated performance parameters are energy and power abilities, charge and discharge capabilities at different current rates. Furthermore, these parameters have been examined at different working temperatures (60 °C, 40 °C, 25 °C, 0 °C and −18 °C). The experimental results reveal that the type of lithium-ion capacitor used in this work has an energy density about 14 Wh/kg, which is two and half times higher than the used EDLC. These results also indicate similar properties as the electrical double-layer capacitors in the terms of internal resistance and state of charge determination. In contrast to EDLCs, the results show that lithium-ion capacitors suffer considerably at the low temperatures due to lower energy at high current rate. The same characteristics can be observed during discharge phase, due to the occurrence of the Peukert effect.

Moreover, series of tests have been carried out at different state of charge values. Here we have found that the capacitance has a polynomial relationship against a linear equation for EDLC and it seems in function of applied current rates.

From the point of view of the power capabilities, several approaches have been investigated based on the EDLC and battery methodologies. The results reveal that the power density according to EDLC method is about 1200 W/kg with a pulse efficiency of 90%. However, the W/kg based on the battery method during 2 s pulse is about 500 W/kg.

Furthermore, a life cycle test has been done based on the load profile as reported in the forthcoming ISO 12405-2 standard. The preliminary results figure out that the life cycle of the lithium-ion capacitors is decreased with 3.4% till 1400 cycles. Then forward, the capacity reduction is stabilized until 4000 cycles.

1. Introduction

Due to increasing gas prices and environmental concerns, battery propelled electric vehicles (BEVs) and hybrid electric vehicles (HEVs) have recently drawn more attention. In BEV and HEV configurations, the rechargeable energy storage system (RESS) is a key design issue [1–3]. So, the system should be able to have good performances in terms of energy density and power capabilities during acceleration and braking phases. However, the thermal stability, charge capabilities, life cycle and cost can be considered also as essential assessment parameters for battery system.

From the point of view of battery management system, the estimation of the state of charge of the RESS can be assumed as a possible evaluation factor.

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Presently batteries are used as energy storage devices in most applications. These batteries should be sized to meet the energy and power requirements of the vehicle. Furthermore, the battery should have good life cycle performances. However, in many BEV applications the required power is the key factor for battery sizing, resulting in an overdimensioned battery pack [4,5] and less optimal use of energy [4]. These shortcomings could be solved by combination of battery system with electrical double-layer capacitors [6–8].

In [9] it is documented that such hybridization topologies can result into enhancing the battery performances by increasing its life cycle, rated capacity, reducing the energy losses and limiting the temperature rising inside the battery. Omar et al. concluded that these beneficial properties are due to the averaging of the power provided by the battery system [4,6,9].

However, the implementation of EDLCs requires a bidirectional DC–DC converter, which is still expensive. Furthermore, such topologies need a well-defined energy flow controller (EFC). Price, volume and low rated voltage (2.5–3 V) hamper the combination of battery with EDLCs [6,10].

In order to overcome these difficulties, Cooper et al. introduced the UltraBattery, which is a combination of lead-acid and EDLC in the same cell [11]. The new system encompasses a part asymmetric and part conventional negative plate. The proposed system allows to deliver and absorb energy at very high current rates. The UltraBatteries have been tested successfully in the Honda Insight. However, this technology is still under development.

In the last decade, a number of new lithium-ion battery chemistries have been proposed for vehicular applications. In [12–15] is reported that the most relevant lithium-ion chemistries in vehicle applications are limited to lithium iron phosphate (LFP), lithium nickel manganese cobalt oxide (NMC), lithium nickel cobalt aluminum oxide (NCA), lithium manganese spinel in the positive electrode, lithium titanate oxide (LTO) in the negative electrode.

According to the results in [14,15] we can observe that most of these batteries cannot yet fulfill the United Stated Advanced Battery Consortium (USABC) criteria regarding life cycle: 500–1500 cycles against 5000 [16]. Moreover, the thermal stability of NMC and NCA based batteries can yet not be guaranteed. Then, the cost of the NMC, NCA and LTO based batteries is in the range of 400–1000 $/kWh, which exceed the USABC goals of 200 $/kWh [16].

In the last few years, a new energy storage technology has been developed, the so-called hybrid capacitors also known as lithium-ion capacitors (LiCap). These are devices where one of the electrodes is carbon activated and the other consists either of a pseudo-capacitance material or of an alloy like that used in a battery [17]. Due to this combination, the energy density can be enhanced and the life cycle performances are still very high.

In 2009 Sojitz Corporation and Taiyo Yuden Co., ltd made an investment for development and commercialization of Advanced Capacitor Technologies [18]. According to the news release, the new developed LiCap will have an energy density about 25 Wh/kg. The higher energy density is due to the higher capacitance of the cell which is 5000 F. However, there is not enough information available regarding these LiCap.

In 2001, Amatucci proposed a new hybrid capacitor concept consisting of an activated carbon in the positive electrode and lithium titanate oxide in the negative electrode [19]. By combination of these two electrodes, the energy density of the system can be enhanced up to 10–15 Wh/kg and the long life cycle can be guaranteed. Due to the used nanomaterial, the system exhibits high rate performances.

Following this work, in 2004 Yoshino replaced the lithium titanate oxide based electrode by a graphite or hard carbon electrode [20]. In order to pre-charge the anode electrode, a lithium ion electrode has been inserted. Although, the operating voltage of this system is significantly higher, the experimental results reveal that the energy density is in the same range.

Furthermore, Wang et al. investigated the $LiMn_2O_4$ and $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ in the negative electrode for hybrid lithium-ion capacitors in an aqueous system [21,22]. Another work performed by Vasanthi et al., the cathode electrode $LiCoPO_4$ with olivine structure has been analyzed in a non-aqueous electrolyte [23]. However, none of these reported electrodes could achieve the mentioned long life cycle, with exception of lithium titanate oxide.

Following these works, Karthikeyan et al. proposed a new hybrid capacitor concept fabricated with the crystal structure $LiFeSiO_4$ in the negative electrode and activated carbon in the positive electrode in a non-aqueous $LiPF_6$-EC/DMC electrolyte [24]. According to the preliminary results, the novel hybrid capacitor can achieve 43 Wh/kg. However, the power capabilities of the system seems very poor compared to the previous studies: 200 W/kg. Moreover, the cycleability only has been approved till 100 cycles.

In the last years, several Japanese companies started with commercialization of hybrid capacitors for hybrid vehicles and stationary/mobile applications.

In 2005 Fuji Heavy Industries announced a lithium-ion capacitor technology for hybrid applications with an energy density up to 25 Wh/kg [25]. Their LiCap cells consist of a pre-lithiated activated carbon as a negative electrode and activated carbon in the positive electrode. They concluded that these devices offer a compromise of low cost, good performances and long life cycle.

In 2010, the Japanese company Taiyo Yuden commercialized cylindrical hybrid capacitors with an energy density up to 4–10 times higher than the EDLC [26]. The company claims that the power and rate capabilities of the developed cells are comparable to the EDLCs. However, the company offers only 3 capacitances: 40 F, 100 F and 200 F. However, these rated capacities are not suitable for automotive applications.

During the last years, a considerable effort has been done for understanding the chemical behavior of hybrid and asymmetric lithium-ion capacitors. However, the lithium-ion capacitors are relatively new, where the overall electric characteristics are not clear. Especially from the point of view of Battery Management System (BMS), there is till now, no model developed yet for such pre-doped lithium-ion capacitors.

In [17] a number of such hybrid capacitors and lithium-ion capacitors have been investigated, only considering however static parameters such as energy density, power density and internal resistance at room temperature.

Gualous et al. investigated the general characteristics of lithium-ion capacitors based on electrochemical impedance spectroscopy (EIS) [27]. The EIS has the abilities to obtain the main characteristics over a wide frequency range, using however much lower currents than actually occur in hybrid vehicles. Furthermore, these currents have adverse effects on the RESS behavior [12–14].

From the point of view of the modeling, Sikha et al. proposed a mathematical model of lithium-ion capacitors based on electrochemical behavior [28], focusing on the investigation of the electrochemical processes inside the system with its suitability in real applications still under consideration.

In this study the general characteristics of LiCap (see Table 1) are analyzed and compared with EDLC and lithium-ion batteries. The investigated parameters are power density, energy density and

Table 1
General properties of the type of lithium-ion capacitor used in this work.

Voltage/V	2.2–3.8
Capacitance/F	2200
Temperature/°C	−20 to 70
Weight/kg	0.208