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Lithium-ion capacitor – Characterization and development of new electrical model

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ABSTRACT

Due to the wide applications of lithium-ion capacitors (LiCs) in various fields and due to the lack of comprehensive study regarding LiC modeling, there is a need for an accurate electrical model, which can predict the LiC's behavior at different load conditions. Characterization helps better understanding of investigated energy storage system and reveals its functioning range, linear and nonlinear variations and also its limits. As the electrochemical based energy storages are non-linear, the presented model should be linearized in the range of the specific application. Therefore the identification procedures should be performed under various conditions as needed. Results from hybrid pulse power characterization (HPPC) test have been used for the system identification of LiC in the time domain. Since system identification in the time domain cannot provide a complete map of variation of model parameters, a wide range frequency impedance spectroscopy (10 kHz–20 mHz) and at various conditions such as current, state of charge (SoC) levels and temperatures has been performed in order to identify the parameters of assumed model in the frequency domain, which is an unique analysis and never has been performed for lithium ion capacitors. The used model has been chosen based on probable chemical reactions, which occur within a specific frequency range. Frequency domain analysis can identify model variation, which is not possible in time domain identification. In this paper a new identification approach has been introduced based on combination of time and frequency domains. Based on proposed method, identification process in frequency domain helps to identify parameters which are not variable in function of current and SoC variations. Therefore the mentioned parameters can be withdrawn from the cost function in the time domain and it improves the performance of system identification procedure. The proposed method improves the model accuracy around 2% at time domain and around 5% at frequency domain.

1. Introduction

Nowadays due to increasing demand for high energy and high power storage systems in different applications such as electric vehicles, uninterrupted power supplies and communication devices, hybrid lithium ion capacitors (LiC) are getting increased attention. A lithium ion capacitor is a hybrid energy storage device, which combines the mechanism of lithium ion batteries with the cathode of an Electric double-layer capacitor (EDLC) [1]. The positive electrode is composed of activated carbon and negative one is formed by lithium-ion doped carbon, which causes higher cell capacity compared to EDLC [2–18]. Furthermore, this device provides higher energy, power density, output voltage and also a wide range of operating temperatures from −30 °C to 70 °C [19]. In addition, cycle life performance of LiC is much better than for batteries; due to these mentioned characteristics; they are suitable for applications that need high power, energy density and excellent durability. Since they have high power performances and are higher energy-optimized than EDLCs, there is no need for additional electrical storage, which reduces the costs. For instance, LiCs can be used in high power transportation applications such as electric tracks and buses, energy storage for renewable energy plants and power quality and power electronic applications.

In Ref. [20] it is mentioned that EDLCs can improve the battery performances by increasing its life cycle and available capacity as well as reducing the energy losses and limiting the temperature rising inside the battery. In Refs. [21,22] it is documented that these advantageous characteristics are due to the averaging of the power provided by the battery system. However, the implementation of hybrid capacitors still requires power electronic converters, which

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are expensive and complicated. According to Refs. [22,23] price and low terminal voltage (2.5–3 V) are barriers to development of battery-EDLC combinations in traction applications. In order to overcome these difficulties, Cooper et al. introduced the Ultra Battery, which is a combination of lead-acid and EDLC in the same cell [24]. The new topology consists of a part asymmetric and a conventional negative plate. It delivers and absorbs energy at very high current rates. The Ultra Batteries have been tested successfully in the Honda Insight. However, this technology is still under development.

In Refs. [25–28] a number of lithium-ion battery chemistries have been proposed for vehicular applications. The most relevant batteries are lithium iron phosphate (LFP), lithium nickel manganese cobalt oxide (NMC), lithium nickel cobalt aluminum oxide (NCA), lithium manganese spinel in the positive electrode, and lithium titanate oxide (LTO) in the negative electrode [53]. However, the thermal stability of NMC and NCA based batteries is not guaranteed yet. The cost of the NMC, NCA and LTO batteries is in the range of 400–1000 $/kWh, which is relatively high compared to the objectives as specified by United States Advanced Battery Consortium (USABC) [29].

Ref. [30] describes the development and commercialization of Advanced Capacitor Technologies. According to the results, the new developed LiC 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.

In Refs. [2,3] the authors proposed a new hybrid capacitor concept consisting of an activated carbon in the positive electrode and lithium titanate oxide $Li_4Ti_5O_{12}$ (LTO) in the negative electrode. In the suggested topology, the energy density of the system has been improved up to 10–15 Wh/kg and a long life cycle has been achieved as well. As the power capability of the LiC is limited by the negative electrode, several appropriate materials have been evaluated. In Refs. [4–8] semi crystalline graphite has been used [9,10], proposed graphite, prelithiated graphitic carbon is suggested in Refs. [13–16] and Ref. [12] has investigated Li_2FeSiO_4. Furthermore there are other combinations that usually use active carbon as the negative electrode (rarely for positive electrode) and $LiNi_{0.5}Mn_{1.5}O_4$ [31] or graphite [32–35] as the positive electrode. But these types have lower terminal voltage. Also in Ref. [36], authors implemented $LiCoPO_4$ with olivine structure as the cathode electrode.

Another configuration of LiC, which uses active carbon in the both positive and in the negative electrodes, is the so-called dual carbon cells [36,37]. As both electrodes are active carbon, it is expected that they have similar characteristics as batteries. Stoller et al. proposed a new configuration using graphene, which is introduced to both electrodes. A Fe_3O_2/graphene (Fe_3O_2/G) Nano composite with high specific capacity as negative electrode, and a graphene-based three-dimensional porous carbon (3D Graphene) as positive electrode were proposed in Refs. [38,39]. It is reported that the new composition increases the energy density without sacrificing the power density.

In Ref. [40] the performance parameters of few types of LiCs such as power, energy density and internal resistance have been analyzed at room temperature. Authors in Refs. [41–43] have done wide range frequency response analysis (FRA) in order to identify LiC characterization in the frequency domain using electrochemical impedance spectroscopy (EIS). In Ref. [44] different types of LiCs have been cycled at various temperatures ranging between -30 °C and 65 °C and high current level. It is reported that unlike the EDLC, lithium-ion capacitors performance declines at low temperatures, just like lithium-ion batteries. Electrochemical behaviors based on Mathematical models of LiCs have been proposed in Ref. [45]. Significant numbers of literature has investigated electrical modeling and parameter identification of different type of lithium ion batteries in time domain and have developed high order models based on online observers such as extended Kalman filter together with artificial intelligence like neural network and fussy logic [54–57]. While it's not a case for LiC as it modeled by simple 1st order equivalent circuit based models [17].

1.1. Contribution of the paper

In this paper a comprehensive study of new type prismatic lithium-ion capacitors has been performed. The new version provides a higher rated capacitance up to 3300 F and also a higher energy density around 20 Wh/kg. In addition to the experiments and electrical modeling of the mentioned cell at different temperatures and current levels in time and frequency domains, the previously presented electrical model has been improved. Based on mathematical theories like Mittag-Leffler, the new proposed model for LIC converted to time domain which makes model implication in real-time softwares possible. Furthermore, the proposed model has been validated at various thermal conditions and load profiles. The paper focuses on the combination both identification methods (time and frequency), increasing the efficiency of the identification process in order to highlight the advantages of each method and to overcome the drawbacks. As this approach has not been subject to significant research, the proposed methodology is unique and never has been used before.

1.2. Organization of the paper

The remainder of the paper is organized as follows: In section 2, lithium-ion capacitor is characterized and its mechanism and chemical structure has been discussed. Model parameters based on a new equivalent circuit in frequency domain have been identified in section 3. Based on Mittag-Leffler method, the complicated frequency model simplified and converted to time domain. The model performance in both time and frequency domain is evaluated and validated. And finally in section 4 a new methodology for parameter estimation based on combination of time and frequency domain system identification is proposed and validated.

2. Chemistry and characterization

Lithium-ion capacitors can be categorized between EDLCs and lithium-ion batteries. Basically they belong to the class of hybrid capacitors or asymmetric capacitors. Same as EDLCs, porous activated carbon is used as cathode. The specific capacitance of the cathode is about 100 F/g, which is assumed based on 1000 m^2/g for the surface area of the electrode and 0.1 F/m^2 for the double-layer. The anode employs carbon material with significant doped lithium-ion and the electrolyte contains Li salt. Fig. 1 compares chemical structures of EDLC, LiCs and lithium-ion batteries.

Doped lithium improves the energy density remarkably in comparing with EDLCs. Fig. 2 shows the structure of prismatic lithium capacitors. Anode and cathode laminates, containing porous current collectors, are placed alternately and are separated by separator panels. Lithium foil adjacent to the anode and is directly connected through the copper tabs. After injecting the electrolyte, pre doped lithium starts dissolving into the electrolyte and moving to the anode due to its lower potential. The potential of the anode remains low because of the use of lithium absorbing carbon that is pre-doped with lithium while the potential of the cathode rises and falls. In the case of EDLCs, the voltage of the cathode and anode vary symmetrically as activated carbon is used for both electrodes. This can describe why the energy density of LiCs is higher than the EDLCs due to their higher nominal voltage.

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