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Review article

Hybridization of rechargeable batteries and electrochemical capacitors: Principles and limits

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ABSTRACT

The demand for electrochemical energy sources is nowadays extremely large and it addresses very different application, from small portable devices, over electric vehicles, to large stationary applications. The requirements for the electrochemical energy sources are therefore extremely various in terms of cost, specific power and energy, cycle life, safety. In spite of the large variety of electrochemical energy storage systems available today they may not fulfil all of the requirements requested. The need of achieving both high energy density and power density has been pointed out in the last decade and, among the different possible approaches, the hybridization of two types of electrochemical energy storage devices, rechargeable battery and electrochemical double layer capacitor, has been strongly investigated. This work reviews the different approaches to the hybridization, such as internal and external, serial and parallel and provides a collection of today's achievements.

Contents

1. Introduction

Reliable energy storage is a prerequisite for using renewable energy in remote locations, the integration into the electricity system and the development of a future decentralized energy supply system. Electrochemical energy storage in batteries or electrochemical capacitors provides a reasonable section of all energy storage technologies storing kinetic, potential, chemical, magnetic, or thermo-chemical energy [1]. The wide scenario of the electrochemical energy storage devices accounts for several different systems with particular properties. Two main classes of systems can be considered: (i) the non-rechargeable systems which are assembled in the charged state and which are exhausted when

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the reactants are consumed, and (ii) the rechargeable systems which can, indeed, be effectively recharged for a certain number of times. The rechargeable systems can again be sorted into two groups: the electrochemical capacitors and the rechargeable batteries.

Electrochemical capacitors are characterized by the highest specific power within the rechargeable electrochemical energy storage devices, typically above 10 kW kg^{-1} and a low specific energy, typically below 10 Wh kg^{-1} [2,3]. The large majority of the electrochemical capacitors described in literature are the so-called electrochemical double layer capacitors (EDLCs) which charging process is purely electrostatic and ideally it does not involve any charge transfer [2,3]. The active material typically used in EDLCs is a high surface area carbon, such as activated carbon, templated carbon, or carbon nanostructures [4]. The charging mechanism in the ideal case is purely electrostatic. The double layer (DL) at the high surface area electrode/electrolyte interface is charged upon polarization and the charge injected in the solid electrode is compensated by the mirror charge accumulated in the DL. This process is fast and therefore EDLCs can provide higher specific power compared to rechargeable batteries. The rate of the DL charging is typically limited by the electrolyte conductivity and the pore structure of the electrode [5]. The charge accumulation in a high surface area carbon electrode via double layer formation is limited to the surface and therefore the specific charge and the specific energy are limited. The specific surface area of the active material cannot be increased indefinitely and therefore other strategies to increase the specific energy of EDLC have to be found. Another class of systems usually ascribed as electrochemical capacitor is that of the redox capacitor.

An example of this technology is the polyacene capacitor [6], also called polyacene battery, where polyacene is used as active material on both electrodes. These systems are commercially available and produced, for example, by the Japanese company Taiyo Yuden Energy Device Company [7].

The active material of a redox capacitor is charged via an electrochemical reaction but the charge transfer reaction is so fast that the charging characteristic of those systems is comparable to that of EDLCs. Conductive polymers are the materials mostly proposed for redox capacitors. Redox capacitors could be properly described also as rechargeable batteries [2,3].

Rechargeable batteries, also called secondary batteries, are a group of systems typically characterized by a relatively high specific energy and low specific power. In spite of the many different chemistries that can be applied to develop a rechargeable battery, all the systems have important similarities. The electrode active materials are typically different on the positive and on the negative electrode and the charging process of these materials is in all cases a reversible faradaic reaction associated to a certain redox couple which typically involves at least one solid species. The kinetic of the charging/discharging process of a rechargeable battery therefore involves solid state diffusion processes and/or precipitation/dissolution of solid phases. Rechargeable batteries can use either an aqueous or an organic solvent. On the contrary of EDLC the charging mechanism of rechargeable batteries involves the bulk of the electrode material and therefore the specific energy is much higher.

The most important rechargeable systems are the lead-acid battery, the nickel metal hydride battery and the lithium battery. It is beyond the purpose of this article to review all of the available types of batteries, which are well described in literature [8–11]. The aim of this publication is to discuss and to compare the different approaches to the hybridization of rechargeable batteries and electrochemical capacitors. The various routes towards the hybridization described in the scientific literature are compared and critically discussed.

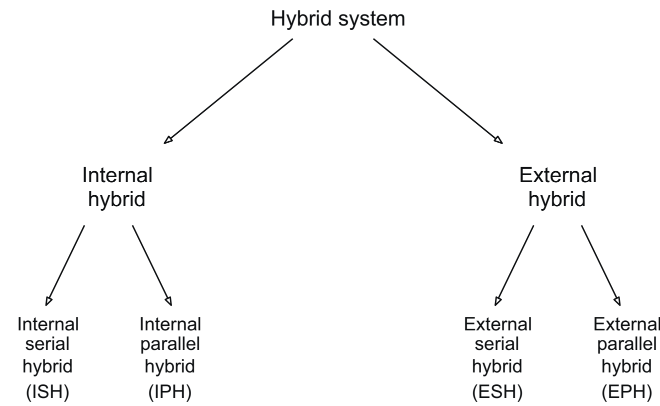

Fig. 1. Schema of possible approaches to the hybridization of electrochemical capacitors and rechargeable batteries.

2. Approach to the hybridization of electrochemical capacitors and batteries

The hybridization of electrochemical capacitors and rechargeable batteries has been proposed and discussed by several authors in the last decades. Many different approaches utilizing many different materials have been discussed but there is no unambiguous definition of an electrochemical hybrid energy storage device. A simple sorting of possible electrochemical capacitor–rechargeable battery hybrid systems is proposed in Fig. 1. The hardwired connection of a ready available electrochemical capacitor and a ready available rechargeable battery is defined as an “external hybrid”. Such a connection can be arranged in a serial way where the electrochemical capacitor is electrically connected in series with the battery resulting in “external serial hybrid” device (ESH), or they can be connected in a parallel arrangement giving an “external parallel hybrid” device (EPH).

A similar way of hybridization may be imaged at the internal level, in this case the “internal hybrid” devices are developed by the hybridization on the electrode level. Therefore, a device based on a battery electrode and an electrochemical capacitor electrode will be defined as an “internal serial hybrid” (ISH).

These kind of systems were firstly named “asymmetric electrochemical capacitors” shortened in “asymmetric capacitor” and introduced in [12]. The term “hybrid capacitor” was introduced and trademarked by Evans Capacitor Company to describe an electrolytic capacitor using a pseudocapacitive negative electrode [13]. The name “lithium-ion capacitor”, sometimes abbreviated in “lithium capacitor” was introduced to describe a device using a graphite negative electrode and an activated carbon based positive electrode in combination with a Li^+ containing electrolyte. Nowadays however these names and other are often misused in the scientific literature to describe various internal hybrids.

The parallel hybridization of electrochemical capacitors with batteries at the internal level in an “internal parallel hybrid” (IPH) consists in the realization of a device where both electrodes contain electrochemical capacitor and battery materials. These kind of electrodes can be defined as bi-material electrodes [14]. In terms of internal hybridization ISH and IPH represent two extreme cases and intermediate situations can be proposed, for example systems with one bi-material electrode and one regular battery or electrochemical capacitor electrode. The division between the different approaches is straightforward, and there is no ambiguity in the case of the external hybridization. However the classification in case of the internal hybrid might be more complicated due to the different materials that can be used. In this context all the materials which are mainly charged by a faradaic reaction are considered “battery