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Mechanisms and Designs of Asymmetrical Electrochemical Capacitors

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ABSTRACT

Different charge storage mechanisms in electrochemical energy storage devices are reviewed, including non-Faradaic capacitive, Faradaic capacitive, Faradaic non-capacitive, and their combinations. Specifically, Faradaic capacitive (pseudocapacitive) storage and Faradaic non-capacitive (Nernstian) storage are attributed to the transfer of delocalised and localised valence electrons, respectively. Mathematical and graphical expressions of the respective storage performances are presented. The account is made especially for asymmetrical electrochemical capacitors (AECs), supercapattery and supercabattery. Both hypothetical and experimental examples are presented to demonstrate the merits of supercapattery that combines capacitive and Nernstian electrodes. Enhanced storage performance is shown by properly pairing and balancing the properties of the negatrode (negative electrode) and positrode (positive electrode) in the AEC or supercapattery. In addition, the design, laboratory manufacturing and performance of several stacks of bipolarly connected AEC cells are assessed in terms of commercial feasibility and promise.

1. Introduction

Supercapacitor is the commercial name of electrochemical capacitor (EC) that has attracted exponentially growing interests in both academia and industry. The positrode (positive electrode) and negatrode (negative electrode) of an EC can be made from the same or different materials, corresponding to, respectively, symmetrical or asymmetrical EC [1–3]. Strictly speaking, there is no EC that is symmetrical because even with the same material, the charge storage processes are different at the positrode and negatrode. For example, when charging an EC with activated carbon on both electrodes, anions are stored in the positrode whilst cations in the negatrode, which means asymmetry in the electrical double layer (EDL) structure, charge storage kinetics and specific capacitance. Thus, it can be stated that all known ECs are asymmetrical in nature.

Nevertheless, the scientific rigour is not always followed in research, and a successful advancement in science or technology may also result from initially misinterpreted observations [4]. It is very much a similar story in the research and development of ECs, particularly the asymmetrical device which often has an electrode that is capable of Faradaic charge storage to gain an increased specific capacity of storage. The Faradaic process is known to involve transfer of charges (electrons or ions or both) across the "electrode | electrolyte" interface (EEI). It has been ascribed to Nernst's law concerning a unique electrode potential, E^o, although its association with the so called pseudocapacitance in recent years has led to confusion between materials with capacitive and non-capacitive performances. There is no doubt that enhancement in energy storage is the practical purpose in both cases, but clarification of the charge storage mechanisms is necessary so that researchers can inform their industrial colleagues with reliable information about energy storage capacity, speed and cycle life. This article aims to offer some fundamental considerations and practical examples on using both capacitive and non-capacitive materials to fabricate asymmetrical ECs. With particular reference to hybrid devices whose performances follow or do not follow the capacitor equations, the terms of *supercapattery* and *supercabattery* are recommended, respectively, together with correct performance description and analysis [2,3]. Furthermore, device engineering leading to the fabrication of stacked EC cells will be briefly considered. It is acknowledged that the terms "pseudocapacitor" and "hybrid capacitor" are also used in the literature, but these terms are not the same as supercapattery

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because the former is still a capacitor and is composed of two different capacitive electrodes. A supercapattery can be composed of two different capacitive electrodes, but also of a capacitive and a Nernstian electrode as explained below in details.

2. Charge storage mechanisms in electrodes

In general, storage mechanisms can be classified as either non-Faradaic capacitive, Faradaic capacitive (pseudocapacitive) or Faradaic non-capacitive (Nernstian) (see Fig. 1a) [3]. Based on these mechanisms, the electrochemical properties of electrodes which could be used in the fabrication of ECs can be categorised under any of the four schematic illustrations given in Fig. 1b. The schematic cyclic voltammograms of Fig. 1b represents single electrode characterisations (i.e. collected using the three-electrode cell configuration).

Fig. 1(b4) could be used to generally illustrate the electrochemical characteristics of electrodes displaying non-Faradaic capacitive storage i.e. EDL capacitance. This is usually due to the electrostatic separation of electrons and ions at the EEI. Fundamentally, the amount of interfacial charge storage (Q) in these types of electrodes can be correlated with the interfacial

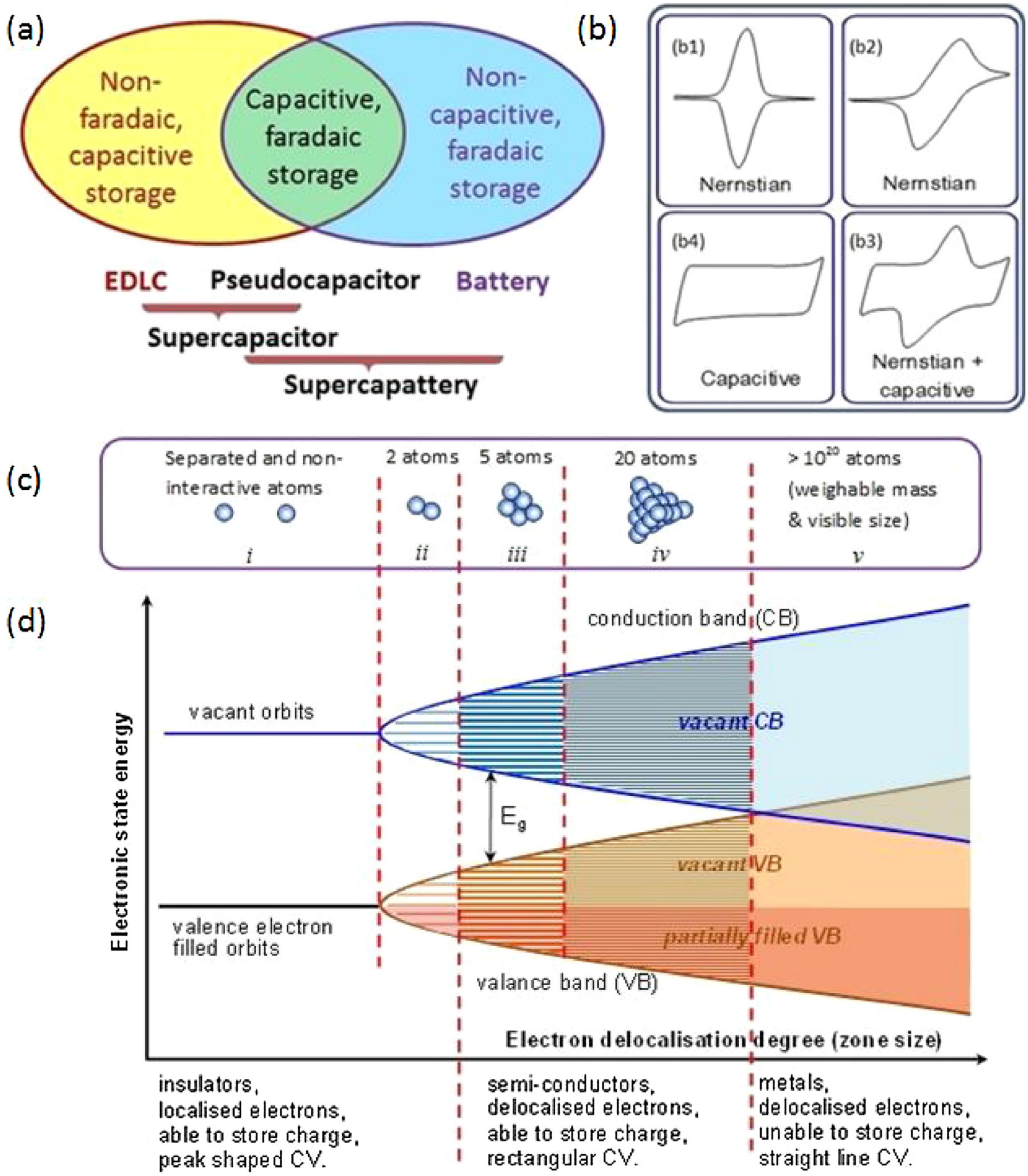

Fig. 1. **(a)** Charge storage mechanisms for electrochemical energy storage and their possible device classification [3]. **(b)** Schematic representations of the voltammetric features for Nernstian (b1, b2), mixed Nernstian and capacitive (b3) and capacitive (b4) charge storage mechanisms. **(c)** Schematic illustrations of the band model for chemical bonding between metal atoms that are separated and non-interactive (i), and forming clusters of 2 (ii), 5 (iii), 20 (iv) and 10^{20} (v) atoms. **(d)** The corresponding energy levels of the valence electrons as a function of the degree (or zone size) of delocalisation of valence electrons in the respective clusters of metal atoms [11,24].