



How the electrochemical reversibility of a battery-type material affects the charge balance and performances of asymmetric supercapacitors



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ABSTRACT

The charges stored within the pseudocapacitive materials are strongly affected by the charge-discharge rate because of their electrochemical reversibility, especially when employing a battery-type material in the asymmetric design. As a result, the charges stored in the positive and negative electrodes in asymmetric supercapacitors (ASCs) are usually not well balanced because of the wide-rate operation of ASCs. This work demonstrates how to construct an ASC with one electrode material of the battery type through the charge balance consideration using the nickel hydroxide/activated carbon (Ni(OH)₂/AC) system as an example. Due to the fact that the electrochemical reversibility of Ni(OH)₂ is worse than that of AC, the influences of the current density (at 0.5 and 80 A g⁻¹) in evaluating the charge capacity of Ni(OH)₂ on the cell capacitance, power ability, and stability of the ASC are investigated. The above parameters of this ASC are evaluated by cyclic voltammetric, constant current charge-discharge, and electrochemical impedance spectroscopic analyses. The proposed charge capacity has been demonstrated to be an important factor for determining the specific energy, power ability, and stability of ASCs. A general strategy for achieving the optimal performances of an ASC with one battery-type electrode is proposed in this work.

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1. Introduction

The increasing global energy demand highlights the urgency in developing and improving alternative clean energies and their storage technologies. Currently, one of the major research efforts focuses on how to use promising techniques to construct environmentally friendly, high-performance systems to enhance and maximize the energy storage capacity. In this field, supercapacitors (SCs) have been widely investigated for decades owing to many aspects of applications, such as hybrid electric vehicles/electric vehicles, starting assistance of fuel cells, and power sources of electronics [1,2] with a wide range of specific energy and power. The promising potential of SCs is due to their extremely high charge-discharge rate and ultra-long cycle performance [3,4].

According to the mechanisms of charge storage, SCs of the double-layer type usually consist of highly porous materials such as activated carbons, carbon nanotubes, or graphene with very

high specific surface area [5–8] which can store energy due to solvent/ion rearrangements/adsorption in the electrical double layers. On the other hand, pseudocapacitors utilize metal oxides or conducting polymers with several oxidation states/structures in the potential window of solvent decomposition to store electricity through very fast Faradaic redox reactions [8]. To extend the cell voltage, dissimilar materials with complementary working potential windows have been designed to assemble the so-called SCs of the asymmetric type (i.e., asymmetric supercapacitors, denoted as ASCs) [9–14].

Recently, a lot of investigations focus on extending the cell voltage in order to enlarge the specific energy of ASCs. However, finding the suitable operation condition of ASCs, especially for the system consisting of one battery-type electrode, which is vital for the long-term usage and safety concern, is still a challenge [15–17]. For example, our previous work demonstrated the importance of the electrochemical reversibility of the battery-type materials on the cell capacitance retention and energy efficiency of resultant ASCs at various power rates [18]. Moreover, the enhanced specific energy of such a “capattery” usually comes with the tradeoff in the specific power and cycle life [19–22]. Therefore, how to improve the desired functions of ASCs with a battery-type electrode is of both practical and academic interests. The desired functions of supercapacitors, at least, include enhanced specific energy and

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power, long cycle life, wide operation temperature region, etc. In comparing with rechargeable batteries, the extremely high charge rate, ultra-long cycle life, wider operation temperature range, and better safety of SCs are the promising advantages [3,4,17].

2. Concept description

Fig. 1(A) shows the schematic diagram between cell capacitance (C_{cell}) and specific power for EDLCs and ASCs with one electrode of the battery type. In general, the cell capacitance and power ability of SCs are mainly determined by the positive or negative electrode materials with slower electrochemical kinetics [8]. Furthermore, the electrochemical kinetics of pseudocapacitive materials in ASCs is generally slower than that of the double-layer type, leading to their worse capacitance rate-retention. Here, a new parameter, capacitance rate-retention, R , is defined as follows:

$$R (\%) = \frac{C_{s,t,i}}{C_{s,t,o}} \times 100\% \quad (1)$$

where $C_{s,t,i}$ and $C_{s,t,o}$ are indicative of the specific capacitance of an electrode material measured at a current density of i and a reference current density of i_o (or at a scan rate of v and a reference scan rate of v_o). This parameter, strongly affected by the electrochemical reversibility of pseudocapacitive materials, is expected to be closely related to the dependence of cell capacitance on specific power of resultant cells since the cell capacitance obeys the following equation:

$$\frac{1}{C_{cell}} = \frac{1}{C_{s,t,+}} + \frac{1}{C_{s,t,-}} \quad (2)$$

where $C_{s,t,+}$ and $C_{s,t,-}$ indicate the specific capacitance of positive and negative electrodes, respectively. Note that the specific

capacitance of a battery material is extremely large because of its narrow potential window and significant charge of redox reaction(s) [11]. In addition, C_{cell} of an ASC will approach the specific capacitance of the double-layer type electrode if the battery-type electrode exhibits extremely large specific capacitance according to equation (2). Therefore, the enhanced specific energy of a “capattery” is attributable to the simultaneous increase in cell voltage and capacitance. However, from the worse capacitance rate-retention of the battery material (e.g., 7% for Ni(OH)₂ as the scan rate of CV increases from 1 to 500 mV s⁻¹ [11]), the decay in cell capacitance of such ASCs is much faster than that of EDLCs (see Fig. 1(A)), leading to the significant loss in the specific energy and power at high rates without considering the tradeoff in cycle life [19–22]. The above phenomenon emphasizes the key role played by the electrochemical reversibility of the pseudocapacitive materials in the ASCs. On the other hand, the full utilization of active materials on both positive and negative electrodes at a wide current density region with the largest cell voltage is also desirable because of the possible achievement to the highest specific energy [23,24]. This target, unfortunately, conflicts the usage of the battery materials due to the possible loss in most specific capacitance at the high power operation. Moreover, how to evaluate the charges stored on the battery-type electrode becomes a concern in constructing such ASCs because charge balance between positive and negative electrodes has been demonstrated to determine the cell voltage of ASCs in our previous work [24].

In order to clarify the above concern and concept, the scheme representing two electrode materials with very different capacitance rate-retention properties is shown in Fig. 1(B). Curve 1 shows the electrode materials with typically high reversibility since their capacitance is weakly dependent on the charge-discharge current density or scan rate of CV. On the other hand, curve 2 shows the

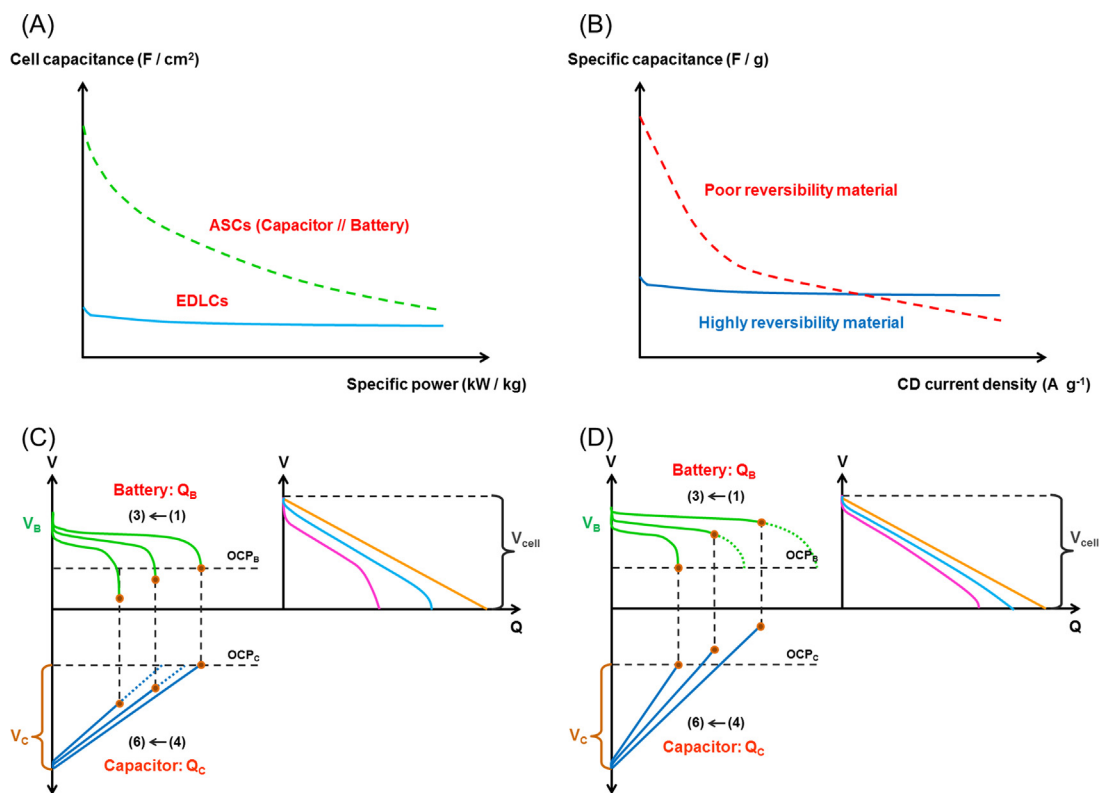


Fig. 1. (A) The schematic diagram demonstrates the difference for the dependence of cell capacitance (C_{cell}) on the specific power of EDLCs and ASCs with one electrode of the battery type. (B) The scheme represents two electrode materials with very different capacitance rate-retention properties. Sketch for (left) the discharge curves of (1–3) battery-like and (4–6) capacitor-like electrodes and (right) the resultant discharge curves of an asymmetric cell at three current densities when the charge-balanced condition was estimated at (C) low and (D) high current densities.

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