



Aqueous based solid battery-capacitor asymmetrical system for capacitive energy storage device



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HIGHLIGHTS

- Aqueous and solid battery-capacitor asymmetrical systems are developed for energy storage.
- The asymmetrical system use Zn as negative electrode and CNT as positive electrode.
- The asymmetrical energy storage systems are capacitive with up to 1.6 V operating voltage.
- The all-solid asymmetrical Zn-CNT capacitor exhibited 10,000 CV cycles with good stability.

ARTICLE INFO

Article history:

Received 11 February 2017

Received in revised form

7 September 2017

Accepted 7 October 2017

Available online 9 October 2017

Keywords:

ASC
Zinc
CNT
Solid
Battery-capacitor

ABSTRACT

Battery-capacitor asymmetrical systems, using Zn as battery-type negative electrode and CNT as capacitor-type positive electrode are developed with both aqueous and solid polymer based electrolytes. The devices combine the merits of both electrodes: The Zn electrode contributed 1.6 V cell voltage, while the CNT electrode results in fast and reversible capacitive behavior. An all-solid asymmetrical system is demonstrated using a PVA-TEAOH polymer electrolyte and exhibit high power capability and long cycle life. The good capacitive behavior, excellent stability upon 10,000 cycles of charge and discharge, and high cell voltage suggest a promising system for thin film solid energy storage applications.

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1. Introduction

Most current electrochemical capacitors (ECs) are symmetrical with two identical carbon based electrodes. In spite of performance advantages such as high power and long cycle life, limited energy density has always been an issue for extending the applications of such systems [1]. Significant efforts have been devoted to increase the range of applications by expanding the operating voltage and thus energy density, leveraging organic electrolytes and ionic liquids electrolytes with wider chemical stability or asymmetric supercapacitors (ASCs) with different negative and positive electrodes. ASCs can be categorized into (a) redox//redox type (b) redox//double layer type and (c) double layer//double layer type [2]. ASCs in redox//double layer type are interesting, since the negative and positive electrodes operate in different potential

windows, enabling wider voltage than that of symmetric devices [3].

Among the redox//double layer type ACSs, many using carbon double-layer materials (e.g. carbon nanotube, graphene, or activated carbon) as one electrode and pseudocapacitive transition metal compounds (e.g. MnO_2 and V_2O_5) as the other electrode [4–7] have been developed. These exhibit improved energy density over symmetric. Battery electrodes can also provide high voltage and high energy density [8]. Hybridization with battery electrodes could leverage the merits of both ECs and batteries: The battery-type electrode is able to increase the open-circuit and operating voltages, thus increasing energy density while the capacitor-type electrode enables high power density and long cycle life. Most research on battery-capacitor ASCs focuses on Li-ion capacitors in organic electrolytes [9–12]. Compared to organic electrolytes, aqueous electrolytes are not only more conductive but also more stable in air, thus enabling low-cost processing and handling [13]. Battery-capacitor ASCs using an aqueous electrolyte have great

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potential for enhanced safety, better environmental friendliness, and lower cost over organic based devices [14].

Most of the current ASCs rely on liquid electrolytes (aqueous, organic, and ionic liquid electrolytes in liquid state) [4–7,9–12]. All-solid EC devices are superior to conventional liquid electrolyte-based devices in terms of safety, reliability, weight, flexibility, and ease of handling [15]. In this work, we leverage both asymmetric configuration and aqueous-based polymer electrolytes to develop a solid battery-capacitor redox//double-layer type ASC using a zinc battery-type negative electrode and a carbon nanotube (CNT) capacitor-type positive electrode. The CNT was used as a proof of concept, which could be altered to other carbon based materials such as graphene and activated carbons or pseudocapacitive electrodes. We started with a liquid system and then migrated to a solid system. While both ASCs demonstrated high voltage, high energy density, and low cost, the solid battery-capacitor ASC offers advantages particularly in cycle life, safety, and portability.

2. Experimental

A thin titanium foil (0.13 mm, McMaster-Carr) was used as current collector for both the Zn negative electrode and the CNT positive electrode. Ti foil was ultrasonically cleaned for 5 min each in acetone, methanol, and DI water. A CNT ink, composed of 64 wt.% multi-wall CNT, 21 wt.% graphite, and 15 wt.% poly vinyl alcohol (PVA) was applied as the positive electrode [16]. A Zn ink, composed of 45 wt.% Zn powder, 45 wt.% ZnO powder, 5 wt.% PVDF, and 5 wt.% carbon black was applied as the negative electrode. Both electrodes were prepared by doctor blade casting of the respective precursor inks. A 35 wt.% tetraethylammonium hydroxide (TEAOH) liquid electrolyte and a Poly vinyl alcohol (PVA)-TEAOH electrolyte that contained 81 wt.% TEAOH and 19 wt.% PVA solid polymer electrolyte [17] were used as electrolyte for liquid and solid battery-capacitor ASCs, respectively. PVA-TEAOH polymer electrolyte was applied here for improving the environmental stability and film integrity over conventional PVA-KOH electrolyte. The detailed characterizations of the PVA-TEAOH polymer electrolyte were reported elsewhere [17–19].

The liquid ASCs were assembled using a CNT positive electrode and a Zn negative electrode and separated by a sheet of 140 μm thick filter paper soaked in 35 wt.% TEAOH (referred to as liquid cell). The solid ASCs utilized the same electrodes but with a ca. 140 μm thick layer of TEAOH-PVA solid polymer electrolyte (referred to as solid cell). Both liquid and solid cells had an apparent surface area of 1 cm^2 . Electrochemical characterizations such as cyclic voltammetry (CV), charge-discharge (CD), electrochemical impedance spectroscopy (EIS), and cycle life test via CV were conducted in ambient conditions (i.e. 25 $^{\circ}\text{C}$ and ~40% humidity) using an Ivium CompactStat. The potential tracking of electrodes in a cell set-up was assisted by a GW-Instek GDS-122 oscilloscope [20]. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were conducted on a FEI Quanta FEG 250 environmental scanning electron microscope (ESEM) equipped with EDX.

3. Results and discussion

To understand the operation mechanism of the battery-capacitor ASC, both positive (CNT) and negative (Zn) electrodes were first studied separately in a 3-electrode setup. Then a liquid cell using these two electrodes was assembled and characterized. Solid cells were subsequently developed and characterized to demonstrate the performance of this ASC in the solid state.

3.1. Individual electrode characterizations

The potential window of the CNT electrode in 35 wt.% TEAOH was determined through an incremental CV scan as shown in Fig. 1a, proceeding from 0 V to high potentials at an 0.05 V increment. The CV profiles were rectangular, indicating an ideal capacitive behavior until up to 0.3 V, where the oxygen evolution peak became significant. Thus 0.25 V vs. Hg/HgO was determined as the positive potential of the CNT electrode in TEAOH electrolyte. Within the potential region, the electrode was scanned at various scan rates (Fig. 1b). The current density increased linearly with the scan rates (i.e. 0.1, 0.5 and 1 mA cm^{-2} at 10, 50, and 100 mV s^{-1} , respectively). All CV profiles at these scan rates exhibited an ideal rectangular shape, suggesting a fast charge storage on CNT.

Zn battery electrode was used for its significant negative potential (–1.35 V vs. Hg/HgO) in strong alkaline environment. The negative potential was leveraged for a high cell voltage. The CV profile of the Zn negative electrode showed a clear redox couple (Fig. 1c), resulting from electrochemical reactions between metallic Zn and Zn(OH)_2 . The reaction occurs in a strong alkaline environment on the electrode-electrolyte interface and can be expressed by equation (1) [21]:



The reduction peak of the electrode was not as sharp as the oxidation peak due to hydrogen evolution at low potentials. Various CD current densities corresponding to those CVs in Fig. 1b (0.1, 0.5, 1 mA cm^{-2} or 0.1, 0.5, 1 A g^{-1}) were applied to examine the kinetics of the Zn electrode (Fig. 1d). The potential at a low current density (i.e. 0.1 mA cm^{-2}) was almost constant at –1.35 V, while the difference in potential between charging and discharging increased slightly at higher current densities, suggesting the kinetics of the Zn electrode was fast enough to match the CNT electrode at these scan rates. Testing of the individual electrodes indicated a good match in terms of potential windows between CNT and Zn electrodes for an ASC.

3.2. Liquid cell characterizations

A liquid cell was assembled using CNT as positive electrode and Zn as negative electrode in 35% TEAOH to study the behavior of these two electrodes in an ASC. The liquid cell was examined at 10, 50, and 100 mV s^{-1} CV scan rates. The electrochemical behavior of the cell (Fig. 2a) was similar to an EC since the capacity of the Zn electrode was much higher than that of the CNT electrode, and therefore, the latter dominates cell capacitance according to (equation (1)):

$$1/C_{\text{cell}} = 1/C_+ + 1/C_- \quad (\text{equation 1})$$

where C_{cell} , C_+ , and C_- represent the capacitance of the cell, the positive CNT electrode, and the negative Zn electrode, respectively. The calculated areal capacitance at 10 mV s^{-1} for the liquid cell (Fig. 2a) was 8.2 mF cm^{-2} , which is very close to the 8.5 mF cm^{-2} measured for the CNT electrode (Fig. 1b) at the same scan rate. This suggests a minimum equivalent capacitance of 230 mF cm^{-2} from the Zn electrode, which translates to a 1:27 ratio between CNT and Zn. While the cell may not be “balanced” and did not reach the maximum energy and power density [22], a larger capacity of the Zn electrode protects it from over-charging or discharging. The potential of the Zn electrode was constant at –1.35 V, of which the main role was to boost the cell voltage. Meanwhile, the CNT is the smaller and dominating electrode, the device exhibited a capacitive behavior and was capable to be charged and discharged at various

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