Journal of Power Sources 378 (2018) 209–215

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Aqueous based asymmetrical-bipolar electrochemical capacitor with a 2.4 V operating voltage

Haoran Wu*, Keryn Lian

Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario M5S 3E4, Canada

HIGHLIGHTS

- A novel aqueous asymmetrical-bipolar electrochemical capacitor is developed.
- The system leverages the merits of asymmetrical electrodes and dual-pH electrolytes.
- The devices show capacitive performance with a high operating voltage of 2.4 V.
- The devices exhibit low self-discharging, high efficiency and excellent stability.

ARTICLE INFO

Keywords:
Asymmetrical
Bipolar
Dual-pH electrolyte
Aqueous
Electrochemical capacitor
High voltage

ABSTRACT

A novel asymmetrical-bipolar electrochemical capacitor system leveraging the contributions of a Zn-CNT asymmetrical electrode and a KOH-H_2SO_4 dual-pH electrolyte was developed. The positive and negative electrodes operated in electrolytes with different pH, exploiting the maximum potential of both electrodes, which led to a cell voltage of 2.4 V. The potential tracking of both electrodes revealed that the Zn negative electrode could maintain a potential at −1.2 V, while the CNT positive electrode can be charged to +1.2 V without significant irreversible reactions. A bipolar ion exchange membrane has effectively separated the acid and alkaline from neutralization, which resulted in stable performance of the device with capacitance retention of 94% and coulombic efficiency of 99% over 10,000 cycles. This asymmetrical-bipolar design overcomes the thermodynamic limit of water decomposition, opening a new avenue towards high energy and high power density aqueous-based ECs.

1. Introduction

One of the main factors limiting the electrochemical capacitor (EC) applications is their relatively low energy density, despite their high power density and long cycle life [1]. Since both energy and power density are proportional to the square of the maximum operating voltage [2,3], the extension of cell voltage has attracted intensive research, such as using organic electrolytes, asymmetrical electrodes, and dual-pH electrolytes [2,4–13]. Organic electrolytes are typically employed in commercial ECs due to high chemical stability, leading to a device voltage window of typically 2.7 V [14,15]. Aqueous electrolytes are generally more conductive, safer, and cheaper when compared to organic electrolytes [2,16]. Although most symmetrical aqueous based ECs suffer from a limited voltage window of ca. 1.2 V due to water decomposition [15,17], they can be improved by using asymmetrical electrodes or dual-pH electrolytes.

Asymmetrical electrodes in ECs, in which two different materials for positive and negative electrodes with complementary potential windows are used, have been extensively studied [4–11]. A proper asymmetrical design not only increases the maximum voltage of the device, but also adapts the merits of both batteries and ECs, leveraging high capacity from a faradic electrode and fast charge-discharge response from a capacitor-type electrode for higher energy and power density. Typically, the positive electrode relies on redox-active materials, such as PbO_2, $Ni(OH)_2$, or $Co(OH)_2$ for battery-type electrodes or MnO_2, V_2O_5, or RuO_2 for pseudocapacitive electrodes. The negative, capacitor-type electrode is usually based on carbon materials such as carbon nanotubes (CNTs), graphene, or activated carbon (AC) [16,18]. The voltage window of asymmetrical ECs can surpass the 1.2 V limit, due to suppressed O_2 and H_2 evolution on the positive and negative electrodes, respectively. For example, $Ni(OH)_2$-graphene and $Co(OH)_2$-graphene asymmetrical ECs achieved a cell voltage of 1.6 V [19].

Dual-pH electrolytes, recently introduced by E. Frackowiak et al., utilize two aqueous electrolytes with different pH (i.e. acid and

---

* Corresponding author.
E-mail address: haoran.wu@mail.utoronto.ca (H. Wu).

https://doi.org/10.1016/j.jpowsour.2017.12.048
Received 1 October 2017; Received in revised form 30 November 2017; Accepted 17 December 2017

alkaline) for each electrode [12,13]. These devices are constructed in a 3 compartments cell with a buffer solution (i.e., a neutral electrolyte) in between the acid and alkaline solutions. An ion exchange membrane (IEM) was employed to further suppress the cross-diffusion of H^+ and OH^- and to maintain stable pH of the electrolytes [2]. Since the H_2 and O_2 evolution potentials are dependent on the individual electrolytes, the voltage window of the device is the sum of the two electrodes potentials from different pH, which overcomes the thermodynamic limitation of a single electrolyte. Dual-pH electrolytes have been demonstrated using AC-AC symmetrical electrode systems. An impressive voltage of 2.1 V was achieved by employing H_2SO_4 or $LiNO_3$ as positive electrolyte and KOH as negative electrolyte [13]. A modification by X. Wang et al., using a bipolar IEM in H_2SO_4-KOH dual-pH electrolytes, resulted in a stable device voltage of 1.8 V with improved cycle life [2]. The applications of dual-pH electrolytes increased the device voltage and enhanced energy and power density.

In this work, we combined the merits of both asymmetrical electrodes and dual-pH electrolytes and constructed a system using Zn as negative electrode material in a KOH alkaline solution, CNT as positive electrode material in H_2SO_4 acid, and a bipolar IEM as separator. A stable maximum operating voltage of 2.4 V was achieved.

2. Experimental

2.1. Materials

A thin Ti foil was used as the current collector for the CNT based positive electrode. The Ti foil was ultrasonically cleaned for 5 min in methanol and 5 min in DI water. Prior to electrode coating, the Ti surface was cleaned again with isopropyl alcohol (IPA). An aqueous based CNT ink, composed of 64 wt% multi-wall CNT, 21 wt% graphite, and 15 wt% poly vinyl alcohol (PVA), was doctor-bladed on the Ti foil [20]. The electrode was heated at 100 °C for 1 h, allowing the solvent to evaporate. The CNT coating was 40 μm in thickness with a loading of 1 mg cm^{-2}. This translates to an electrode density of 0.25 g cm^{-3}. For the negative electrode, a 25 μm Zn foil with a loading of 18 mg cm^{-2} was used. The Zn electrode was ultrasonically cleaned for 5 min in methanol and in DI water. Since the specific capacity of Zn is 820 mAh g^{-1} [21], the theoretical capacity of the applied Zn electrode is 14.8 mAh cm^{-2}. Both electrodes were protected and insulated by an electrodeposition tape with an apparent area of 1 cm^2 exposed to the electrolyte.

2.2. Cell assembly

3-electrode tests of the CNT positive electrode were conducted in 0.5 M H_2SO_4, 0.5 M Li_2SO_4, and 3 M KOH. Ag/AgCl was used as reference electrode in acid and neutral electrolytes, while Hg/HgO was used for the alkaline electrolyte. All potentials were converted against SHE for comparison. A microbial fuel cell (MFC) configuration (Fig. 1) was utilized for device characterizations with 0.5 M H_2SO_4 in one flask and 3 M KOH in the other. Two commercial IEMs from Membranes International Inc. were laminated as a separator. The cation IEM (CMI-7000) was facing the compartment containing KOH while the anion IEM (AMI-7001) was facing the compartment with H_2SO_4. The Cation IEM only allows K^+ ion diffusion while the Anion IEM only allows SO_4^{2-} ion diffusion. Therefore, the cross diffusion of H^+ and OH^- was minimized and the pH value in each flask was maintained. An Ag/AgCl reference electrode was used only in acid compartment since the voltage drop across the IEM was negligible.

2.3. Electrochemical characterizations

Electrochemical characterizations including cyclic voltammetry (CV), charge-discharge (CD), leakage current density, and electrochemical impedance spectroscopy (EIS) were conducted on an Ivium CompactStat. The potential tracking of each electrode in a cell was measured simultaneously with a voltage scan by an external GW-Instek GDS-122 oscilloscope [22]. The S-value to determine the proper potential window of the CNT positive electrode was calculated via the following equation [23]:

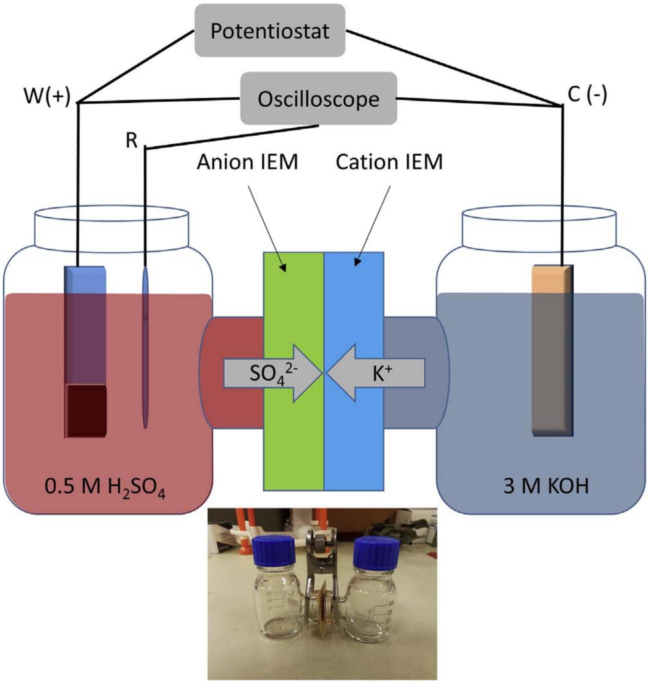

Fig. 1. Schematic of Zn-CNT asymmetrical electrodes in KOH-H_2SO_4 dual-pH electrolytes setup; the inset is a photo of the actual device.

$$S = Q_{charge} / Q_{discharge} - 1$$

where Q_{charge} and $Q_{discharge}$ are the charge accumulated during charging and discharging, respectively. This value can be used to identify the critical potential (i.e. the maximum potential of the electrode) where irreversible reactions such as oxygen evolution (OER) become significant.

3. Results and discussion

3.1. Electrode characterizations

Prior to cell design, the performance of the individual electrodes was characterized in aqueous electrolytes. CNT was used as a positive electrode in solutions with different pH and its maximum potential was determined by incremental potential scans in a 3-electrode setup. The incremental scans were conducted in 3 M KOH (Fig. 2 a), 0.5 M Li_2SO_4 (Figs. 2 b), and 0.5 M H_2SO_4 (Fig. 2 c), starting at the open circuit potentials (OCP) of the CNT electrode in each electrolyte until a significant oxidation current at high potentials was reached. The high current implies the limitation from OER. The maximum potential in each electrolyte can be determined by an S-value [23], in which a value greater than 0.1 represents a columbic efficiency less than 90%. The S-value in Fig. 2 d shows that the maximum potential of the CNT electrode in alkaline, neutral, and acid electrolytes was 0.2 V, 1.0 V, and 1.2 V, respectively (highlighted by green circles in Fig. 2 d). In spite of the variation in potential windows in different electrolytes, the capacitance of the electrode remained the same at ca. 17 mF cm^{-2}.

Since Zn is only stable in alkaline [24], which was used as the negative electrode, the CV profile of the negative electrode was obtained in 3 M KOH (Fig. 3 a). A pair of pronounced peaks corresponding to the redox couple of Zn in strong alkaline media is expressed by (reaction 1)