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Hybrid capacitors utilizing halogen-based redox reactions at interface between carbon positive electrode and aqueous electrolytes

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HIGHLIGHTS

- Aqueous HC is developed with Br-water treatment of activated carbon positive.
- Conventional EDLC is changed into HC just by pretreatment and NaBr electrolyte.
- HC shows no capacitance decay to 100,000 cycles with high coulombic efficiency.
- The HC realizes 1.8 V operation in spite of an aqueous electrolyte.
- 1.8 V HC operation provides higher energy and power even than 2.7 V EDLC.

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ABSTRACT

We propose novel hybrid capacitors (HCs) with electrolyte-involved redox reactions of bromide or iodide species by pretreatment of an activated carbon positive electrode. The treatment is simple; impregnation of pores at an activated carbon fiber cloth (ACFC) as a positive electrode with bromine- or iodine-containing water before cell assembly. The treated positive electrode is applied to a HC cell with a non-treated negative electrode of ACFC and its electrochemical performance is investigated by galvanostatic cycling and leakage current tests. Few studies on such “electrolytic” charge storage systems have provided acceptable capacitor performance because of inevitable self-discharge caused by diffusion of charged species form an electrode to the other one through an electrolyte. Nevertheless, our electrolyte-redox-based HCs show excellent performance without undesirable diffusion of charged species. Moreover, the present HC utilizing a bromide redox system fulfills a practical cell voltage of 1.8 V in spite of an aqueous electrolyte system. This high voltage provides excellent energy density, which is 5 times higher than that in a conventional aqueous electric double-layer capacitor (EDLC), and 1.2 times higher even than that in a 2.7 V-class non-aqueous EDLC, while keeping high charge–discharge rate capability.

1. Introduction

Electrochemical capacitors (ECs) often called supercapacitors, are significant energy storage devices that are considered as an object of important scientific and industrial development. Generally, ECs store much higher energy density than conventional dielectric capacitors, and provide higher power density than lithium-ion batteries [1,2]. Moreover, ECs have long cycle life (>10^6 cycles) that makes them maintenance-free energy storage devices [3–5]. Therefore, ECs have been widely studied for various applications of electric equipment, e.g., automobiles, tramways, buses, cranes, forklifts, and wind turbines.

The amount of energy density (E) accumulated in ECs is proportional to the capacitance (C) and the square of voltage (V) according to the following formula:

$$E = 1/2\, C\, V^2 \qquad (1)$$

The capacitance depends essentially on electrode active material, whereas the operating voltage is limited by the stable voltage window of the electrolyte [6–9]. Although the limiting voltage of aqueous EC systems (the theoretical decomposition voltage of

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water is 1.23 V at pH = 7) is much lower than that of non-aqueous ECs, high power density and high specific capacitance are especially remarkable for aqueous ECs [10–12]. On the basis of their charge storage mechanisms, ECs are categorized mainly into electric double-layer capacitors (EDLCs) and pseudocapacitors [1,11]. In other words, the energy storage capacity of an EC arises either from electric double-layer charging or from pseudocapacitance. Electric double-layer charging is a non-faradic process; electronic charges are accumulated at a space charge layer inside electrode material while equivalent ionic charges are accumulated in the electrolyte close to the electrode surface. On the other hand, pseudocapacitance arises from some faradic reactions at electrode surface and generally shows characteristic capacitance behavior depending on the electrode potential [1,11]. To improve energy density of ECs, carbon materials [13–17], transition metal oxides [6,18–21], and conducting polymers [22–25] are well-known candidates for non-faradic as well as faradic storage. Among the available metal oxides, RuO_2 has the highest specific capacitance (~1000 F g^{-1}), but would have a prohibitive price as massive electrode material; a vehicle-sized EC with RuO_2 may cost more than $1 million [26]. Thus, to design advanced, reasonable ECs, one may find novel charge–discharge mechanisms or new active materials.

In our previous paper, we reported that an EC with the potentiostatic treatment at 70 °C provides much higher capacitance than an EC without the treatment [27]; with an aqueous 3.5 mol dm^{-3} NaBr electrolyte system, the treatment leads to a dramatic increase in the capacitance of a positive electrode. As a result, the EC with the treatment attains 2.4 times higher capacitance than an EC without the treatment in a high voltage region. In the later study [28–30], we found that the treated positive electrode may utilize not only double layer capacitance but also some redox reactions involving Br species such as Br^-, Br_2^- and Br_3^- in the electrolyte [28]. Moreover, we successfully proposed a non-aqueous EC utilizing an ionic liquid electrolyte containing Br^-; in this EC the positive electrode also involves Br species-based capacitance [29,30]. Thus these ECs can be regarded hybrid capacitors (HCs) with a partially faradaic positive electrode and a usual double-layer capacitance-based negative electrode.

Although the above pretreatment is available, long duration is necessary for generating significant capacitance increase. Here we propose a novel aqueous HC utilizing electrolyte redox reactions of bromide ion species by modified treatment of an activated carbon electrode with a short time. This treatment with redox species is based on a simple method: bromine-water impregnation into positive electrode micropores before cell assembly. We also applied iodide redox reactions to such an electrolytic redox-based HC. Few studies [31–33] have so far demonstrated EC or HC utilizing an "electrolyte" charge storage system with high or acceptable performance because of a facile shuttle reaction or diffusion of redox species through an electrolyte between electrodes. In other words, reactive species on an electrode easily migrate to an opposite electrode unless they are effectively immobilized at an electrode. If one can design outstanding EC or HC involving electrolyte redox reaction systems, it may become a great progress of high-energy capacitor technology. In this context, this study is an attempt to realize such high-performance capacitor, which utilizes inexpensive redox systems without expensive nanomaterials nor rare-metal oxides.

2. Experimental

Activated carbon fiber cloths (ACFC: ACC-507-15, Nippon Kynol Inc., its specific surface area: ca. 1300 m^2 g^{-1}) were used as electrode material. The treatment of ACFC with redox species was performed by impregnation with bromine water (Kanto Chemical Co., Inc., bromine content ratio: ~1%) or an aqueous 3.5 mol dm^{-3} sodium iodide (NaI) solution dissolving 1 wt% iodine for the positive electrode (10 mm ϕ, ~10 mg) before cell assembly. A negative electrode (10 mm ϕ, ~10 mg) without the treatment and a glass-fiber filter paper as a separator were concurrently immersed in the following electrolyte for 1 h under a reduced pressure. Employed electrolytes of the bromide redox and iodide redox systems were an aqueous 3.5 mol dm^{-3} sodium bromide (NaBr) solution and an aqueous 3.5 mol dm^{-3} NaI solution, respectively.

Two types of HC cells were used in this study: (i) for evaluating polarization characteristics of positive and negative electrodes, a three-electrode asymmetric cell fabricated with the treated electrode as positive, a non-treated electrode as negative electrodes, and an Ag/AgCl reference electrode, (ii) a two-electrode asymmetric cell with the treated and non-treated electrodes was employed for usual electrochemical measurements. For comparison, we also assembled another three-electrode type cell containing a pair of electrodes without treatment and a reference electrode, as well as another two-electrode symmetric cell with non-treated positive and negative electrodes together with an aqueous 3.5 mol dm^{-3} NaBr solution or an aqueous 1.75 mol dm^{-3} H_2SO_4 solution.

A typical charge–discharge cycling test was carried out in a cell voltage range between 0 or 0.5 and 1.0 V at a current density of 1000 mA g^{-1}. The discharge rate capability of the cells was evaluated in a constant-current (CC) mode at various discharge current densities between 100 and 10,000 mA g^{-1}, immediately after their charging to 1.0 V in a CC mode at 100 mA g^{-1}. The leakage current test at a float voltage of 1.0 V was performed by using the cells charged to 1.0 V. The withstand voltage of the cells was determined by monitoring charge–discharge curves at 1000 mA g^{-1}, with increasing the upper limit of charging voltage from 1.0 to 1.9 V with a 0.1 V-step every 3 cycles. All electrochemical measurements were performed with a Solartron model 1470E multi-stat electrochemical measurement unit at room temperature of 25 °C. Before the present electrochemical measurements, 20-cycle formation was carried out at a current density of 100 mA g^{-1}.

3. Results and discussion

Fig. 1(a) shows typical charge–discharge profile at a current density of 1000 mA g^{-1} for the HC cell utilizing the redox reactions of bromide species; this voltage corresponds to the potential difference between negative and positive electrodes. The present HC cell has the initial voltage of ca. 0.5 V because it consists of two different electrodes: the bromine water-treated positive electrode and the non-treated negative electrode. The discharge curve of the HC cell utilizing redox reactions of bromide species exhibits a negligible switching IR loss, which is similar to that of a symmetric EDLC cell with non-treated electrodes even at a high current density of 1000 mA g^{-1}. It is noteworthy that the charge–discharge duration of the HC cell is about 2.6 times longer than that of a conventional EDLC cell. Moreover, the charge–discharge coulombic efficiency of the HC cell at this current density is above 99.8%. This suggests that the HC cell can provide both high energy and good cycle performance.

To understand each electrode behavior during cycling indicated in Fig. 1(a), the potential variation of both the negative and positive electrodes vs. an Ag/AgCl reference was observed and is shown in Fig. 1(b). An open-circuit potential (OCP) of the positive electrode in the HC cell is ~0.75 V vs. Ag/AgCl reference. This suggests that the bromine-treated electrode already has increased positive charges inside the electrode because of the presence of Br redox species as Br_2 or Br_3^- in the electrode micro-pores [34]. Throughout charging and discharging, the treated positive electrode keeps a stable