



High-performance hybrid supercapacitors enabled by protected lithium negative electrode and “water-in-salt” electrolyte

Ming Zhang^a, Sho Makino^a, Dai Mochizuki^{a,b}, Wataru Sugimoto^{a,b,*}

^a Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano, 386-8567, Japan

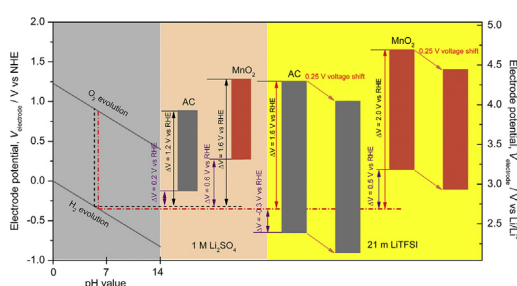
^b Center for Energy and Environmental Science, Shinshu University, 3-15-1 Tokida, Ueda, Nagano, 386-8567, Japan



HIGHLIGHTS

- “water-in-salt” electrolyte and Li are combined to use in hybrid capacitors.
- 4.4 V maximum cell voltage is achieved for hybrid capacitor with MnO₂ electrode.
- 1.8 V voltage window is achieved for hybrid capacitor with AC electrode.
- A hybrid capacitor shows a specific energy of 405 Wh kg_{MnO₂}⁻¹.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Aqueous hybrid supercapacitor
Water-in-salt
Protected lithium negative electrode
Electrochemical stability window

ABSTRACT

Aqueous supercapacitors are attracting increasing attention owing to their high power density, cyclability and environmental friendliness. However, the energy density of common aqueous supercapacitors are restricted by low cell voltage and narrow voltage window. Here we demonstrate that such limitations can be overcome with advanced hybrid supercapacitors using multi-layered water-stable protected lithium negative electrode combined with high concentration “water-in-salt” electrolyte. 4 V-class cell voltage with wide voltage window can be delivered for advanced hybrid supercapacitors with capacitive or pseudocapacitive positive electrodes. A typical advanced hybrid supercapacitor with MnO₂ electrode shows a 4.4 V maximum cell voltage with a 1.5 V window, an energy density of 405 Wh kg_{MnO₂}⁻¹ at a power density of 0.88 kW kg_{MnO₂}⁻¹. A high energy density of 163 Wh kg_{MnO₂}⁻¹ is maintained at a power density of 16.7 kW kg_{MnO₂}⁻¹. These advanced hybrid supercapacitors show acceptable cycle stability and good energy retentions (around 90% within 3000 cycles).

1. Introduction

The demand for new energy systems that have integrated battery-level energy density and electrochemical capacitor-level power density as well as cycle stability is ever increasing. Aqueous hybrid supercapacitors, which typically combine a battery-type faradaic or a pseudocapacitive electrode with a capacitive electrode using an aqueous electrolyte, can bridge the gap between electrochemical double layer capacitors (EDLC) and rechargeable batteries. Such aqueous

supercapacitors may offer an alternative energy solution owing to their intrinsically high power density and long cycle life compared to that of batteries [1–5].

The amount of energy (E) accumulated in an aqueous supercapacitor is proportional to the specific capacitance (C) and cell voltage squared (U^2) according to the formula $E = 1/2C(U_{\max}^2 - U_{\min}^2)$ (Fig. S1). Thus, parameters which determine the energy storage in a supercapacitor are deeply dependent on its electrolyte and electrode materials [6]. The usable cell voltage is determined by the electrochemical

* Corresponding author. Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano, 386-8567, Japan.
E-mail address: wsugi@shinshu-u.ac.jp (W. Sugimoto).

stability window of the electrolyte and the catalytic activity of the electrode materials in the electrolyte, while the capacitance depends on the electrode materials used [7]. Although carbonaceous materials enable working in organic electrolytes, the charge storage process is limited by its accessible surface area, resulting in limited specific capacitance [8–10]. As opposed to the capacitive charge storage mechanism, pseudocapacitive metal oxides (for example, MnO_2 [11–14] and RuO_2 [15,16]) involve near surface confined faradaic reactions, resulting in relatively high specific capacitance. To achieve a good energy performance for aqueous supercapacitors, it is critical that high specific capacitance and wide voltage window are simultaneously fulfilled. Since the electrochemical stability window of water is limited by the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), the voltage window is typically less than 1.6 V. Enhancement in cell voltage is desired for improvement in energy storage of aqueous supercapacitors to compete with their counterparts with ionic liquid or organic electrolytes. Therefore, to achieve this goal, the negative electrode potential needs to be stable below the cathodic voltage limitation of aqueous electrolyte. At pH 7.0, the cathodic and anodic limits of water decomposition are located at 2.62 V and 3.85 V vs Li/Li^+ , hence hydrogen gas will evolve on the surface of the negative electrode below its cathodic voltage limitation. Thus, the use of energy-dense negative materials such as graphite (0.1 V vs Li/Li^+) and metallic lithium (0 V vs Li/Li^+) are limited to nonaqueous electrolyte. We have previously demonstrated that advanced hybrid supercapacitors that employ aqueous electrolyte with a multi-layered water-stable protected negative electrode consisting of laminated metallic lithium or lithiated graphite, polymer electrolyte and water-stable lithium ion conducting solid electrolyte $\text{Li}_{1+x+y}(\text{Ti,Ge})_{2-x}\text{Al}_x\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (LTAP), can extend the negative electrode potential close to 0 V vs Li/Li^+ , thus providing a cell voltage close to 4 V with aqueous catholytes, making it a competitive alternative for batteries in energy density [12,17–20].

However, the energy storage in these advanced hybrid supercapacitors using aqueous electrolytes is still restricted by the narrow potential window of the positive electrode (1.0 V), which in turn limits the cell voltage window ($U_{\text{cell}} = U_{\text{max}} - U_{\text{min}}$) where $U_{\text{max}} = 3.9$ V and $U_{\text{min}} = 2.9$ V. Thus, expanding the potential window of the positive electrode in the catholyte becomes an important issue to increase the energy density $E = 1/2C(U_{\text{max}}^2 - U_{\text{min}}^2)$. Recently, high concentration “water-in-salt” electrolyte has been shown to significantly extend the voltage window up to 3 V (4.9–1.9 V vs Li/Li^+) and has been utilized for aqueous batteries [21–23]. This dawn hope to improve the energy density of advanced hybrid supercapacitors by extending the potential stability window of the positive electrode material in “water-in-salt” electrolyte. It has recently been demonstrated that a stable potential window of 2.4 V for carbonaceous materials in 5 M (≈ 20 m) LiTFSI can be achieved [8]. LiTFSI is considered to be an ideal salt for “water-in-salt” electrolyte owing to its high solubility in water (> 20 m at 25 °C) and high stability against hydrolysis. The drawback naturally is the cost being more expensive than “salt-in-water” electrolytes, nevertheless, it is less expensive than or comparable to typical ionic liquids or non-aqueous solvents used in supercapacitors. An extended cathode window of about 1.4 V (3.23–4.63 V vs Li/Li^+) and a high specific capacitance of 239 $\text{F g}_{\text{MnO}_2}^{-1}$ for MnO_2 in 5 M LiTFSI has also been realized, thus a useable U_{cell} of 2.2 V could be reached for an asymmetric carbon/ MnO_2 aqueous supercapacitor in “water-in-salt” electrolyte [24]. Nevertheless, the lower potential is limited by the decomposition of the “water-in-salt” electrolyte below 1.9 V vs Li/Li^+ . If the negative potential could be extended to the Li/Li^+ potential, the cell energy density should show a pronounced increase.

Herein, we apply a multi-layered water-stable protected lithium negative electrode and “water-in-salt” electrolyte (21 mol kg^{-1} of aqueous LiTFSI) to expand the cell voltage and usable U_{cell} of hybrid supercapacitors. Advanced hybrid supercapacitors with either capacitive activated carbon or pseudocapacitive MnO_2 electrode can be stably cycled between 4.0 and 2.2 V or 4.4 to 2.9 V with excellent energy

density of 405 $\text{Wh kg}_{\text{MnO}_2}^{-1}$ at a power density of 0.88 $\text{kW kg}_{\text{MnO}_2}^{-1}$.

2. Experimental section

2.1. Preparation of electrolytes

Lithium bis(trifluoromethanesulfonyl)imide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiTFSI, 98%) and inorganic lithium salts ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, LiCl, LiClO_4) were purchased from Wako Pure Chemical Industries. Ultrapure water (UHPLC grade) was purchased from Sigma Aldrich. The LiTFSI electrolyte solutions were prepared by mixing the LiTFSI salt with ultrapure water by molality (mol-salt in $\text{kg-H}_2\text{O}$), which were coded by abbreviated concentrations (m) for 1, 2, 5, 21 mol kg^{-1} of aqueous LiTFSI. 1 mol L^{-1} (M) Li_2SO_4 , LiCl, LiClO_4 were prepared by mixing the inorganic salts with ultrapure water (resistivity $> 18 \text{ M}\Omega \text{ cm}^{-1}$) by molarity (mol-salt in L-solution), respectively. The conductivity of all the electrolytes were measured at room temperature with a conductivity meter (CM-30 R TOA-DKK, Japan).

2.2. Materials synthesis

2.2.1. Synthesis of MnO_2

Manganese dioxide was prepared by chemical co-precipitation via the reaction between KMnO_4 and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$. 2.1 g KMnO_4 (Wako, 99.3%) were dissolved in 100 mL of ultrapure water and kept in an ice bath to avoid any solution overheating. 4.6 g $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (Wako, 99.0%) was dissolved in 100 mL of deionized water. Aqueous $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ was then added drop-wise to aqueous KMnO_4 under stirring. Stirring was kept for 4 h to ensure homogeneous mixing of the solutions. Afterward, the obtained suspension was filtered and washed several times with ultrapure water to remove soluble impurities. The final product was dried at 90 °C for 18 h in air.

2.2.2. Synthesis of composite gel electrolyte

Non-aqueous composite gel electrolyte based on sodium alginate and ionic liquid was prepared with a slightly modified procedure as reported before [25]. First, a 3 wt% aqueous solution of sodium alginate (KIMICA Corporation) was cast on a clean glass plate, then was immersed in a 15 wt% aqueous CaCl_2 solution as a crosslinking agent for 30 min at room temperature. Immediately after gelation, the gel film was washed with ultrapure water and ethanol at least three times. Afterward, the obtained cross-linked gel film was immersed into ethanol with an excess volume for 24 h, followed by immersing in ionic liquid with 0.5 M lithium bis(fluorosulfonyl)imide (LiFSI, ultra dry, 99.9% trace metals basis) in N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide (P13FSI, Kanto Chemicals Co., Ltd). The alginate gel film containing 0.5 mol L^{-1} LiFSI/P13FSI (Alg-LiFSI/P13FSI) was finally obtained by drying at 70 °C for 48 h in a vacuum oven. The thickness of the composite gel electrolyte films was approximately 300 μm .

2.3. Electrode and cell preparation

2.3.1. Preparation of positive electrodes

Two types of positive electrodes were used in the current work: activated carbon (abbreviated as AC, MSP-20, Kansai Coke & Chemicals Co, Japan) and MnO_2 . In a typical preparation of MnO_2 positive ink, 28.26 mg MnO_2 powder and 12.12 mg acetylene black carbon were dispersed in a mixture of 4.9 mL isopropyl alcohol (IPA, Sigma Aldrich)/deionized water (volume ratio of IPA: $\text{H}_2\text{O} = 3:1$), and 100 μL of 5 wt% Nafion solution (Sigma Aldrich). The mixture in a sealed vial was ultrasonic dispersed until a homogeneous mixture was obtained and then IPA/ H_2O mixture was added again into the vial to prepare 10 mL of total ink. Next, the MnO_2 electrode ink was stirred with a magnetic stirrer at room temperature. The MnO_2 positive electrodes were prepared by depositing 5.0 μL of the electrode ink solution onto a

Download English Version:

<https://daneshyari.com/en/article/7725146>

Download Persian Version:

<https://daneshyari.com/article/7725146>

[Daneshyari.com](https://daneshyari.com)