Supporting Materials for

4-V Class Aqueous Hybrid Electrochemical Capacitor with Battery-like Capacity

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1. Experimental details

Preparation of negative electrode:

An ionic conducting poly(ethylene oxide) (PEO)-based polymer membrane of PEO-$Li(CF_3SO_2)_2N$-$BaTiO_3$ was prepared by a casting technique reported previously.[19] PEO (Aldrich, average molecular weight: $6x10^5$) powder, and $Li(CF_3SO_2)_2N$ salt (LiTFSI, Wako) with Li/O=1/18 were completely dissolved in anhydrous acetonitrile. $BaTiO_3$ (Aldrich, 0.1 μm average particle size) was homogeneously dispersed in the PEO and LiTFSI solution with acetonitrile as a filler (10 wt%). The mixture was stirred at room temperature in an N_2-filled dry glove box and was then cast into a clean Teflon dish. The acetonitrile solvent was slowly evaporated at room-temperature in the dry box for 10 h, and was then dried at 110°C for 10 h under vacuum. A water-stable LISICON-type glass ceramic, $Li_{1+x+y}Ti_{2-x}Al_xSi_yP_{3-y}O_{12}$ (x~0.25, y~0.3, 150 μm thick), was supplied by Ohara Inc., Japan. To set up the multilayer water-stable Li electrode, the lithium metal with a Ni thin-film lead, the PEO_{18}-LiTFSI–$BaTiO_3$ composite polymer electrolyte, and the LISICON plate were sandwiched between two pieces of plastic films with low water and gas permeabilities. The cell was evacuated and heat sealed leaving a 5 x 5 mm area window on the LTAP plate.

Preparation of positive electrodes:

MnO_2 powder was prepared following previous reports.[18,21] Fumaric acid ($C_4H_4O_4$, Aldrich) was added to a 0.2 M $KMnO_4$ solution (ultra pure water (> 18 M Ω cm)) in a 1:3 molar ratio while stirring. The resulting sol was degased for 30 min under moderate vacuum and after a few hours, a black gel formed. The gel was washed carefully and dried in air. X-ray diffraction patterns were identical to those reported. The specific BET surface area measured by N_2 gas sorption was 235 m^2 g^{-1}.

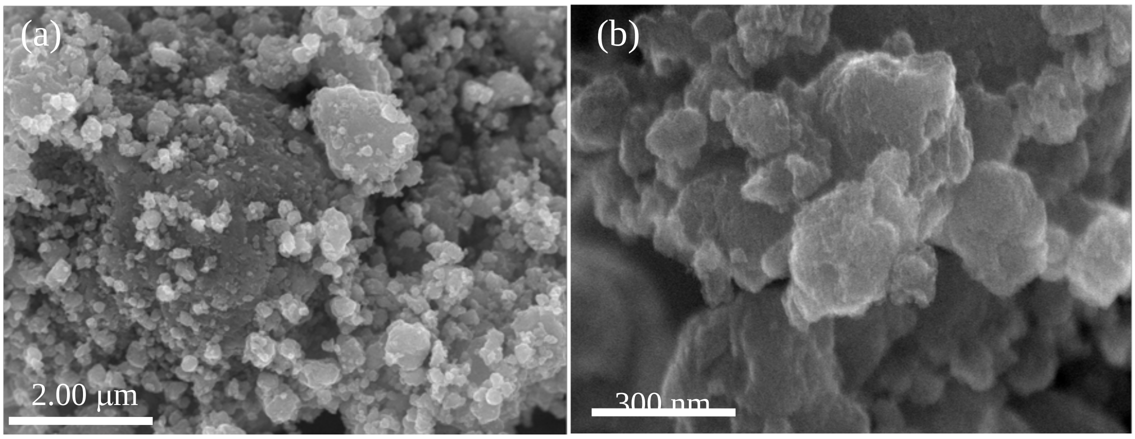

Figure S1. SEM images of MnO_2.

$RuO_2 \cdot 0.5H_2O$ powder was prepared according to literature.[17] Slow controlled addition of a 0.3 M NaOH solution into 0.1 M $RuCl_3 \cdot xH_2O$ solution resulted in precipitation of a black fine powder. The powder was washed thoroughly with ultra-pure water and collected by filtration. Then the powder was heat treated in air at 150°C for 17 h to obtain $RuO_2 \cdot 0.5H_2O$. The capacitance of the material in 0.5 M H_2SO_4 (25°C) at 2 mV s^{-1} was 650 F g^{-1}, in good agreement with literature.

RuO_2 nanosheets were prepared according to literature.[22] α-$NaFeO_2$-structured $NaRuO_2$ was synthesized by heating a mixture of Na_2CO_3 and Ru and RuO_2 (2: 1: 3 molar ratio) at 900°C for 12 h under flowing Ar. The obtained product was treated with aqueous $Na_2S_2O_8$ to prompt oxidative partial de-intercalation of Na ions and then 1 M HCl to exchange the interlayer Na^+ with H^+, resulting in the formation of hydrated layered protonic ruthenate formulated as $H_{0.2}RuO_2 \cdot 0.5H_2O$. Vigorous shaking (at least 10 days) of the acid-treated sample (0.1 g) in 25 cm^3 of aqueous tetrabutylammonium hydroxide results in exfoliation of $H_{0.2}RuO_2 \cdot 0.5H_2O$ into RuO_2 nanosheets. The resultant dark-green suspensions were centrifugated at 2000 rpm for 30 min to separate the exfoliated nanosheets and the readily sedimenting materials.