Room temperature performance of 4 V aqueous hybrid supercapacitor using multi-layered lithium-doped carbon negative electrode

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Abstract

Water-stable multi-layered lithium-doped carbon (Li_xC_6) negative electrode using poly(ethylene oxide) (PEO)-lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) polymer electrolyte containing *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13TFSI) ionic liquid was developed. Electrochemical properties at 60°C of the aqueous hybrid supercapacitor using activated carbon positive electrode and a multi-layered Li_xC_6 negative electrode (Li_xC_6 | PEO-LiTFSI | LTAP) without PP13TFSI exhibited performance similar to that using Li anode (Li | PEO-LiTFSI | LTAP). A drastic decrease in ESR was achieved by the addition of PP13TFSI to PEO-LiTFSI, allowing room temperature operation. The ESR of the multi-layered Li_xC_6 negative electrode with PEO-LiTFSI-PP13TFSI at 25°C was $801 \Omega \text{ cm}^2$, which is 1/6 the value of the multi-layered Li negative electrode with PEO-LiTFSI ($5014 \Omega \text{ cm}^2$). Charge/discharge test of the aqueous hybrid supercapacitor using multi-layered Li_xC_6 negative electrode with PEO-LiTFSI-PP13TFSI at 25°C afforded specific capacity of 20.6 mAh (g-activated carbon)⁻¹ with a working voltage of 2.7-3.7 V, and good long-term capability up to 3000 cycles. Furthermore, an aqueous hybrid supercapacitor consisting of a high capacitance RuO_2 nanosheet positive electrode and multi-layered LiC_6 negative electrode with PEO-LiTFSI-PP13TFSI showed specific capacity of 196 mAh (g- RuO_2)⁻¹ and specific energy of 625 Wh (kg- RuO_2)⁻¹ in 2.0 M acetic acid-lithium acetate buffered solution at 25°C.

Introduction

Electrochemical capacitors, also known as supercapacitors, are electrochemical devices that can store electrical energy at fast charge/discharge rates with long cycle life. Such characteristics have led to implementation of electrochemical capacitors into various products [1,2]. However, the amount of energy that can be stored is considerably lower than present rechargeable batteries [3], since the charge storage is limited to the non-Faradic formation of the electrical double layer at the electrode/electrolyte surface. Enhancement in the energy density of electrochemical capacitors is desired for large-scale applications, for example hybrid vehicles or uninterrupted power sources [3–5]. Commercial electrical double layer capacitors are based on a symmetric configuration of porous carbons for both electrodes and use non-aqueous organic electrolyte such as propylene carbonate or acetonitrile, leading to a cell voltage of ~ 2.5 V. The energy density of electrochemical capacitors is expressed by the following equation, $E = (1/2)C(V_1^2 - V_2^2)$, where E is energy density, C is capacitance and V_1 , V_2 are the higher and lower cut-off voltages of the device during charge/discharge. The energy density can thus be increased by increasing the cell capacitance and voltage, with the cell voltage having a larger impact compared to the capacitance.

The energy density of electrochemical capacitors can be increased by employing an asymmetric configuration combining a porous carbon positive electrode with a lithium-doped carbon (Li_xC_6) negative electrode. The advantage of such devices, known as lithium-ion capacitors (LICs), is the higher cell voltage of ~ 3.8 V as a result of the low standard electrode potential of -2.95 V vs SHE for LiC_6 , leading to energy density of ~ 15 Wh kg^{-1} [6–9]. Li salts dissolved in non-aqueous solvents are used as electrolytes because of the low potential of the negative electrode.

Aqueous hybrid supercapacitors have been studied as alternatives to non-aqueous

devices. Aqueous electrolytes have advantages such as non-flammability and environmental and economic feasibility. However, the smaller potential window (typically ~ 1 V) is a disadvantage in terms of energy density compared to non-aqueous electrolytes [10]. This disadvantage can be overcome by using pseudo-capacitive electrodes with high specific capacitance (up to ~ 1000 F g $^{-1}$) such as RuO $_2$ or such as MnO $_2$ thin films [11]. The cell voltage can be increased up to 2.2 V by the appropriate selection of electrode materials and aqueous electrolytes. For example, hybrid electrochemical capacitors consisting of MnO $_2$ positive electrode with high oxygen evolution over-potential and porous carbon negative electrode in a near neutral electrolyte shows specific energy of 19 Wh kg $^{-1}$ [12,13]. In this case, the cell voltage is thermodynamically limited by the potential of hydrogen evolution at the carbon electrode and oxygen evolution at the MnO $_2$ electrode, thus further increase in the cell voltage is a demanding task.

As an alternate approach, a solid electrolyte can be used to allow the use of lithium metal anode in combination with aqueous electrolytes [14–17]. Such hybrid devices merge the advantages of pseudo-capacitive electrodes, which can only provide high capacitance in aqueous electrolytes, and the low standard electrode potential of Li, which can only be used in non-aqueous electrolytes. The aqueous advanced hybrid supercapacitor (AdHiCap) first reported by the authors utilized water-stable multi-layered Li negative electrode (Li | polymer electrolyte | solid electrolyte | aqueous electrolyte | metal oxides) and affords high specific capacity of ~ 200 mAh g $^{-1}$ and specific energy of ~ 720 Wh kg $^{-1}$ based on the mass of the positive electrodes with cell voltage of 3.7–4.2 V at 60°C [14–16]. A LISICON-type glass ceramic (Li-(Ti,Ge)-Al-Si-P-O) was used as the water stable, lithium conducting glass ceramic. The PEO-LiTFSI polymer electrolyte was used as a buffer layer since direct contact of the Li anode and the glass ceramic leads to undesirable reaction leading to reduction in conductivity. A similar cell configuration using ionic liquid electrolyte instead of polymer electrolyte (PEO-

LiTFSI) was also reported to give specific energy of 170 Wh kg⁻¹ with good cycle life at room temperature [17].

In this study, we pursued the possibility of substituting Li metal with Li-doped carbon and improving the conductivity of the water-stable protected anode by modifying the polymer electrolyte layer. In our previous studies, Li metal was used as the active material for the negative electrode. Lithium metal has a very high theoretical capacity of 3860 mAh g⁻¹ and low standard electrode potential, however, safety and cycle capability caused by dendrite formation may be problematical for practical application. In this work, lithium-doped carbon (Li_xC₆), which has been shown to be practically feasible from lithium-ion capacitor technology, is used instead of Li metal. In addition, an ionic liquid *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13TFSI) was used as an additive to the polymer electrolyte buffer layer to increase the conductivity to allow room temperature operation of AdHiCap.

2. Experimental

Two types of positive electrodes were used, activated carbon (MSP-20, Kansai Coke and Chemicals, Japan) and RuO₂ nanosheet [18] derived from α -NaFeO₂ type NaRuO₂. The activated carbon (AC) positive electrode were prepared by depositing a controlled amount of the active material dispersed in ultra-pure H₂O onto a glassy carbon electrode (5 mm in diameter). The amount of AC deposited was 0.204 mg cm⁻². RuO₂ nanosheet positive electrode was prepared by dropping a colloidal suspension of RuO₂ nanosheet onto the glassy carbon current collector. The amount of RuO₂ nanosheet was 20.4 μ g cm⁻². A thin layer of Nafion ionomer was cast on the electrode as a proton conductive binder. 2.0 M acetic acid buffered solution was prepared by mixing solutions of 2.0 M acetic acid (AcOH) and 2.0 M lithium acetate (AcOLi) in a volume ratio of 12.5:87.5, giving a buffered solution with pH of 5.4.

The Li pre-doped graphite (Li_xC_6) electrode was prepared as follows. Graphite (Sigma-Aldrich Co.), acetylene black and polyvinylidene fluoride (PVDF, Alfa Aesar) were mixed in *N*-methyl-2-pyrrolidone with a mass ratio of 90:5:5. The obtained slurry was coated onto Cu foil (thickness: 20 μm) with a controlled thickness of 107 μm by using doctor blade method. The coated electrode was dried at 60°C for at least 1 hour, and then dried under vacuum at 150°C for 16 hours. The obtained graphite electrode was punched out as a disk (1 cm^2 , 2.3 mg cm^{-2}). A three-electrode stainless cell consisting of graphite working electrode, Li metal foil counter electrode (1 $\text{cm} \times 1\text{cm}$), Li metal reference electrode (2 $\text{mm} \times 2\text{ mm}$), glass-fiber separator (2.4 cm in a diameter; Whatman GF/A) and 1.0 M LiPF_6 in ethylene carbonate and diethylene carbonate (volume ratio of 1:1) (Kishida Chemicals Co., Japan) was used for pre-doping of Li^+ . Pre-doping of Li^+ to graphite electrode was carried out galvanostatically (constant current) to 0 V vs Li/Li^+ or 26 hours at 0.05C using a 580 Battery Test System (Scribner Associate Inc.).

The polymer electrolytes, poly(ethylene oxide) with lithium bis(trifluoromethanesulfonyl)imide (PEO-LiTFSI) and PEO-LiTFSI with *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide ionic liquid ($x\text{PEO-}y\text{LiTFSI-}z\text{PP13TFSI}$; $x:y:z = 18:1:1.5$), were prepared following literature procedures [19–21]. BaTiO_3 was added as a filler to decrease interfacial resistance between $\text{Li/PEO-LiTFSI/LTAP}$ [20].

The multi-layered Li_xC_6 negative electrode was fabricated in a similar manner to multi-layered Li negative electrode [19–22], except that Li_xC_6 was used in place of Li metal. A LISICON-type glass ceramics ($\text{Li}_{1+x+y}(\text{Ti,Ge})_{2-x}\text{Al}_x\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ ($x \sim 0.25$, $y \sim 0.3$); Ohara Inc., Japan, hereafter denoted as LTAP) (10 $\text{mm} \times 10\text{ mm} \times 0.15\text{ mm}$) was used in this work. The anode was either Li or Li_xC_6 , and the polymer electrolyte was PEO-LiTFSI with and without PP13TFSI. The multi-layered negative electrode (Li or $\text{Li}_x\text{C}_6/\text{PEO-LiTFSI}$ or $\text{PEO-LiTFSI-PP13TFSI/LTAP}$) was sealed with aluminum packaging films in an Ar-filled glove box. A 5

mm x 5 mm window was cut out from one side of the aluminum packaging film to expose LTAP to the aqueous electrolyte.

Electrochemical impedance spectroscopy (Solartron 1255B Frequency Response Analyzer with Solartron 1287 Electrochemical Interface) was carried out to evaluate the impedance of the fabricated multi-layered negative electrodes. Impedance spectroscopy was conducted at open circuit potential in a constant voltage mode by sweeping frequencies from 1 MHz to 0.1 Hz at an amplitude of 5 mV. The impedance data was normalized to the geometric area of exposed LTAP on the negative electrode (0.25 cm²). The cell configuration of impedance spectroscopy was such as Li or LiC₆ | PEO-LiTFSI or PEO-LiTFSI-PP13TFSI | LTAP | 1.0 M Li₂SO₄ | Pt mesh in a beaker-type cell at 25 or 60°C.

Charge/discharge tests of Li or Li_xC₆ | PEO-LiTFSI or PEO-LiTFSI-PP13TFSI | LTAP | 1.0 M Li₂SO₄ | AC in a beaker-type cell were conducted by constant current mode using a 580 Battery Test System at 25 or 60°C. The cell potential was controlled with the positive electrode as the working electrode, and the negative electrode as the counter electrode (two-electrode set up). The higher and lower cut-off voltage were set as 3.9 and 2.9 V for the multi-layered Li negative electrode and 3.7 and 2.7 V for the multi-layered Li_xC₆ negative electrode, respectively. The electrode potential of the positive and negative electrode during the charge/discharge was measured with a Ag/AgCl/KCl(sat.) electrode. The specific charge was calculated from the discharge curves and normalized based on the mass of the positive electrode. The specific energy was obtained by integration of the area of the discharge curve in a plot of cell voltage against specific capacity. Although the equation of $(1/2)C(V_1^2 - V_2^2)$, where C is capacitance, V_1 is the higher cut-off voltage and V_2 is the lower voltage cut-off voltage, is commonly used for calculating the energy density electrochemical capacitor, this equation is not applied in this work to avoid overestimation of specific energy due to the slight non-linearity of the discharge curves (non-constant C value).

3. Results and discussion

3.1. Capacitive behavior of aqueous hybrid supercapacitor using multi-layered Li_xC_6 negative electrode at 60°C.

Pre-doping of Li^+ to graphite electrode was carried out galvanostatically at 0.05C from open circuit potential to 0 V vs Li/Li^+ in a three-electrode cell (Fig. 1). After pre-doping, the cell was disassembled in an Ar gas filled glove box and the Li_xC_6 electrode (gold colored) was carefully removed and re-assembled into the multi-layered Li_xC_6 negative electrode (Scheme 1). The resistance of the multi-layered Li and Li_xC_6 negative electrodes was measured by electrochemical impedance spectroscopy in a beaker-type cell consisting of Li or Li_xC_6 | PEO-LiTFSI | LTAP | 1.0 M Li_2SO_4 | Pt cell at 60°C. A small semicircle in the high frequency range and a larger semicircle in the medium frequency range was observed (Fig. 2). An equivalent circuit reported for multi-layered Li negative electrodes [21], was adopted to analyze the impedance spectra using a nonlinear least-squares fit program. The intercept of the high frequency semicircle with the real axis provides the bulk resistance (R_{bulk}), which includes the resistance of 1.0 M Li_2SO_4 electrolyte and bulk resistance of LTAP and PEO-LiTFSI membrane. The small high frequency semicircle corresponds to the grain boundary resistance (R_{grain}) of LTAP and PEO-LiTFSI membrane. The second medium frequency semicircle is attributed to the interfacial resistance ($R_{\text{interface}}$) that consists of the interfacial resistance of Li_xC_6 /PEO-LiTFSI/LTAP and the charge-transfer resistance ($R_{\text{c-t}}$) for the half-cell reaction of Li_xC_6 . These values are summarized in Table I. The total resistance (R_{total}) of the multi-layered Li_xC_6 negative electrode was $146 \Omega \text{ cm}^2$, which is slightly lower than the multi-layered Li negative electrode ($175 \Omega \text{ cm}^2$). The lower $R_{\text{interface}}$ for the multi-layered Li_xC_6 negative electrode ($R_{\text{interface}}=57 \Omega \text{ cm}^2$) compared to the multi-layered Li negative electrode ($R_{\text{interface}}=78 \Omega \text{ cm}^2$) is the major contributor to the decrease in R_{total} . The lower $R_{\text{interface}}$ for Li_xC_6 /PEO-LiTFSI may be due to the

better contact interface of Li_xC_6 with the polymer electrolyte since Li_xC_6 powder has higher roughness compared to a flat Li foil.

Fig. 1. Chronopotentiogram of graphite electrode during Li^+ pre-doping process in 1.0 M $\text{LiPF}_6/\text{EC-DEC}$ (1:1) at 0.05 C.

Scheme 1. Schematic representation of the assembly of aqueous hybrid supercapacitor with multilayered Li_xC_6 negative electrode **after** Li^+ pre-doping process.

Fig. 2. Impedance spectra of Li (circles) and Li_xC_6 (triangles) | PEO-LiTFSI | LTAP | 1.0 M Li_2SO_4 | Pt at 60°C and the equivalent circuit used to fit the experimental data.

The constant current (0.102 mA cm^{-2}) charge/discharge curves of the hybrid supercapacitors in a beaker-type flooded cell with multi-layered Li and Li_xC_6 negative electrodes and AC positive electrodes in 1.0 M Li_2SO_4 at 60°C are compared in Fig. 3(A). The voltage profile exhibited ideal capacitive behavior between 2.9-3.9 V and 2.7-3.7 V for the multi-layered Li and Li_xC_6 negative electrodes, respectively. The 0.2 V difference in cut-off voltage comes from the difference in the electrode potential of multi-layered negative electrodes. The electrode potential of the multi-layered Li negative electrode changes between -2.68 to -2.71 V vs RHE while that of multi-layered Li_xC_6 negative electrode swings between -2.33 to -2.46 V vs RHE during the charge/discharge (blue lines in Fig. 3). This corresponds well with the difference in the electrode potential of the half-cell reactions $\text{Li} \rightarrow x\text{Li}^+ + xe^-$ and $\text{Li}_x\text{C}_6 \rightarrow x\text{Li}^+ + xe^- + \text{C}_6$. The electrode potential of the AC positive electrode (red lines in Fig. 3) fluctuates between 0.370-1.25 V vs RHE, just within the oxygen evolution thermodynamic

limit. The cell using multi-layered Li_xC_6 negative electrode gave a specific capacity of 27.1 mAh g^{-1} and specific energy of 84.4 Wh kg^{-1} , based on the mass of the AC positive electrode. These value are reasonable considering the reported specific capacitance of activated carbon electrode in three-electrode configuration [14].

Fig. 3. Charge/discharge curves at (A) 0.102 and (B) 1.53 mA cm^{-2} for Li_xC_6 (solid line) and

Li (dashed line) | PEO-LiTFSI | LTAP | 1.0 M Li₂SO₄ | AC at 60°C. Left axis: cell voltage in two-electrode configuration (black). Right axis: potential of AC positive electrode (red) and Li_xC₆ and Li negative electrode (blue).

As shown by the charge/discharge curves at a higher current density of 1.53 mA cm⁻² (Fig. 3(B)), the *IR* drop of the cell originates mainly from the multi-layered Li_xC₆ negative electrode; the *IR* drop of cell and negative electrode were 0.772 V and 0.723 V, respectively. The equivalent series resistance (ESR) can be calculated from the following equation; $ESR = \Delta V / \Delta I$, where ΔV is the *IR* drop, and $\Delta I = |I_{\text{charge}}| + |I_{\text{discharge}}|$. The ESR of the multi-layered Li_xC₆ negative electrode was 129 Ω cm², which is in good agreement with R_{total} obtained from impedance spectroscopy (146 Ω cm²). Based on the above analysis, the hybrid supercapacitor employing the multi-layered Li_xC₆ negative electrode shows performance comparable to that using Li.

3.2. Capacitive performance and cycle capability of aqueous hybrid supercapacitor using multi-layered Li_xC₆ negative electrode with PEO-LiTFSI-PP13TFSI at room temperature.

The high ESR of the multi-layered Li_xC₆ negative electrode is the reason for the cell having to be warmed to 60°C and poses a serious problem for high power applications. It has been reported that the addition of PP13TFSI ionic liquid to PEO-LiTFSI with a molar ratio of PP13TFSI:PEO increases the conductivity (2.3×10^{-5} S cm⁻¹ at 25°C) and leads to low interfacial resistance [23]. This approach was also adopted for the multi-layered Li_xC₆ negative electrode. Figure 4 shows the impedance spectra of the multi-layered Li_xC₆ negative electrode with and without addition of PP13TFSI at 25°C. The values of the various resistance are summarized in Table I. R_{grain} and $R_{\text{interface}}$ of Li_xC₆ | PEO-LiTFSI-PP13TFSI | LTAP was considerably decreased when compared with Li | PEO-LiTFSI | LTAP, hence leading to a much

lower R_{total} (913 compared to 5064 $\Omega \text{ cm}^2$ at 25°C).

Fig. 4. Impedance spectra of $\text{Li}_x\text{C}_6 \mid \text{PEO-LiTFSI-PP13TFSI} \mid \text{LTAP}$ (circles) and $\text{Li} \mid \text{PEO-LiTFSI} \mid \text{LTAP} \mid 1.0 \text{ M Li}_2\text{SO}_4 \mid \text{Pt}$ (triangles) at 25°C.

Table I. Summary of resistance analyzed from electrochemical impedance spectroscopy and galvanostatic charge/discharge curves.

	Temperature / °C	Resistance / $\Omega \text{ cm}^2$					ESR / $\Omega \text{ cm}^2$
		R_{bulk}	R_{grain}	$R_{\text{interface}}$	$R_{\text{c-t}}$	R_{total}	
$\text{Li}_x\text{C}_6 \mid \text{PEO-LiTFSI}$	60	65	17	57	7	146	129
$\text{Li} \mid \text{PEO-LiTFSI}$	60	66	16	78	14	175	151
$\text{Li} \mid \text{PEO-LiTFSI}$	25	82	2820	2150	12	5064	5010
$\text{Li}_x\text{C}_6 \mid \text{PEO-LiTFSI-PP13TFSI}$	25	83	148	523	159	913	801

The charge/discharge curves at 0.102 mA cm^{-2} of the hybrid supercapacitor ($\text{Li}_x\text{C}_6 \mid \text{PEO-LiTFSI-PP13TFSI} \mid \text{LTAP} \mid 1.0 \text{ M Li}_2\text{SO}_4 \mid \text{AC}$) at 25°C are shown in Fig. 5. The cell could be cycled between 2.7-3.7 V and showed good capacitive behavior even at 25°C by the addition of PP13TFSI. Long-term cycling test of the hybrid supercapacitor ($\text{Li}_x\text{C}_6 \mid \text{PEO-LiTFSI-PP13TFSI} \mid \text{LTAP} \mid 1.0 \text{ M Li}_2\text{SO}_4 \mid \text{AC}$) at 25°C was conducted by charge/discharge test at 0.102 mA cm^{-2} up to 3000 cycles. The specific capacity as a function of cycles are shown in Fig. 6. The retention of capacity after 3000 cycles was 81%, which is much better than that using multi-layered Li negative electrode at 60°C in our previous work [14]. After 3000 cycles, the electrode potential of the negative electrode drifted to a more positive value. This may be due to the partial irreversibility of the Li^+ (de)intercalation into graphite. The ESR of the negative electrode after long-term cycling increased from 801 to $1510 \Omega \text{ cm}^2$.

Fig. 5. Charge/discharge curves of $\text{Li}_x\text{C}_6 \mid \text{PEO-LiTFSI-PP13TFSI} \mid \text{LTAP} \mid 1.0 \text{ M Li}_2\text{SO}_4 \mid \text{AC}$ at 0.102 mA cm^{-2} at 25°C . Solid line: 1st and 2nd cycles. Dashed line: 2999th and 3000th

cycles. Left axis: cell voltage in two-electrode configuration (black). Right axis: potential of AC positive electrode (red) and Li_xC_6 negative electrode (blue).

Fig. 6. The specific capacity and the retention ratio as a function of cycles for Li_xC_6 | PEO-LiTFSI-PP13TFSI | LTAP | 1.0 M Li_2SO_4 | AC at 0.102 mA cm^{-2} at 25°C during long-term test.

3.3. High specific capacity and high specific energy performance of aqueous hybrid supercapacitor combining RuO_2 nanosheet positive electrode and multi-layered Li_xC_6 negative electrode with PEO-LiTFSI-PP13TFSI in 2.0 M acetic acid buffer solution at 25°C .

RuO_2 nanosheet exhibits excellent pseudo-capacitive behavior with specific capacitance exceeding 900 F g^{-1} in 2.0 M acetic acid buffer solution with pH 5.4 [16,24]. In order to demonstrate the performance of AdHiCap using metal oxide with high capacitance, RuO_2 nanosheet was employed as the positive electrode. Multi-layered Li_xC_6 negative electrode with PEO-LiTFSI-PP13TFSI and 2.0 M acetic acid buffer solution was used as the aqueous electrolyte. Charge/discharge curves of the AdHiCap (Li_xC_6 | PEO-LiTFSI-PP13TFSI | LTAP | 2.0 M AcOH-AcOLi (25°C) | RuO_2 nanosheet) at 0.036 mA cm^{-2} is shown in Fig. 7. The slope of the charge/discharge curve for the positive electrode was non-linear due to the reversible pseudocapacitive behavior in 2.0 M AcOH-AcOLi [16,24]. The obtained specific charge and energy based on the mass of the positive electrode were 196 mAh g^{-1} and 625 Wh kg^{-1} ,

respectively. These values are comparable to hybrid supercapacitors consisting of RuO₂ nanosheet or thin film MnO₂ positive electrode and multi-layered Li negative electrode at 60°C [15,16] and ~ 4 times higher than an aqueous hybrid supercapacitor with similar configuration using MnO₂ positive electrode at 25°C [17].

Fig. 7. Charge/discharge curve at 0.036 mA cm⁻² for Li_xC₆ | PEO-LiTFSI-PP13TFSI | LTAP | 2.0 M AcOH-AcOLi | RuO₂ nanosheet at 25°C. Left axis: Cell voltage in two-electrode configuration (black). Right axis: potential of RuO₂ nanosheet positive electrode (red) and Li_xC₆ negative electrode (blue).

4. Conclusions

A water-stable, multi-layered lithium-doped **carbon** negative electrode was developed for application towards aqueous hybrid supercapacitors. The multi-layered Li_xC₆ negative electrode employing LiTFSI doped PEO with addition of an ionic liquid (Li_xC₆ | PEO-LiTFSI-PP13TFSI | LTAP) at 25°C exhibited comparable performance to a multi-layered Li negative electrode without PP13TFSI addition at 60°C (Li | PEO-LiTFSI | LTAP). Charge/discharge tests of an aqueous hybrid supercapacitor using the newly developed multi-layered Li_xC₆ negative

electrode with PEO-LiTFSI-PP13TFSI at 25°C showed good capacitive behavior and long-term capability. In addition, an aqueous hybrid supercapacitor employing RuO₂ nanosheet positive electrode (Li_xC₆ | PEO-LiTFSI-PP13TFSI | LTAP | AcOH-AcOLi | RuO₂ nanosheet) showed excellent specific capacity of 196 mAh (g-RuO₂)⁻¹ and specific energy of 625 Wh (kg-RuO₂)⁻¹ at 25°C.

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Reference

- [1] J.R. Miller, A.F. Burke, Electrochemical capacitors: Challenges and opportunities for real-world applications, *Electrochem. Soc. Interface* 17 (2008) 53–57.
- [2] J.R. Miller, P. Simon, MATERIALS SCIENCE: Electrochemical Capacitors for Energy Management, *Science* 321 (2008) 651–652. doi:10.1126/science.1158736.
- [3] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nat. Mater.* 7 (2008) 845–854. doi:10.1038/nmat2297.
- [4] P. Simon, Y. Gogotsi, B. Dunn, Where Do Batteries End and Supercapacitors Begin?, *Science* 343 (2014) 1210–1211. doi:10.1126/science.1249625.
- [5] B. Dunn, H. Kamath, J.-M. Tarascon, Electrical Energy Storage for the Grid: A Battery of Choices, *Science* 334 (2011) 928–935. doi:10.1126/science.1212741.
- [6] A. Yoshino, T. Tsubata, M. Shimoyamada, H. Satake, Y. Okano, S. Mori, S. Yata, Development of a Lithium-Type Advanced Energy Storage Device, *J. Electrochem. Soc.* 151 (2004) A2180–A2182. doi:10.1149/1.1813671.
- [7] G.G. Amatucci, F. Badway, A. Du Pasquier, T. Zheng, An Asymmetric Hybrid Nonaqueous Energy Storage Cell, *J. Electrochem. Soc.* 148 (2001) A930–A939. doi:10.1149/1.1383553.
- [8] S.R. Sivakkumar, A.G. Pandolfo, Evaluation of lithium-ion capacitors assembled with pre-lithiated graphite anode and activated carbon cathode, *Electrochim. Acta* 65 (2012) 280–287. doi:10.1016/j.electacta.2012.01.076.
- [9] W.J. Cao, J.P. Zheng, Li-ion capacitors with carbon cathode and hard carbon/stabilized lithium metal powder anode electrodes, *J. Power Sources* 213 (2012) 180–185. doi:10.1016/j.jpowsour.2012.04.033.
- [10] K. Naoi, S. Ishimoto, J. Miyamoto, W. Naoi, Second generation “nanohybrid supercapacitor”: Evolution of capacitive energy storage devices, *Energy Environ. Sci.*

- 5 (2012) 9363–9373. doi:10.1039/c2ee21675b.
- [11] K. Naoi, P. Simon, New materials and new configurations for advanced electrochemical capacitors, *Electrochem. Soc. Interface* 17 (2008) 34–37.
- [12] J.W. Long, D. Bélanger, T. Brousse, W. Sugimoto, M.B. Sassin, O. Crosnier, Asymmetric electrochemical capacitors—Stretching the limits of aqueous electrolytes, *MRS Bull.* 36 (2011) 513–522. doi:10.1557/mrs.2011.137.
- [13] T. Brousse, M. Toupin, D. Bélanger, A Hybrid Activated Carbon-Manganese Dioxide Capacitor using a Mild Aqueous Electrolyte, *J. Electrochem. Soc.* 151 (2004) A614–A622. doi:10.1149/1.1650835.
- [14] S. Makino, Y. Shinohara, T. Ban, W. Shimizu, K. Takahashi, N. Imanishi, W. Sugimoto, 4 V class aqueous hybrid electrochemical capacitor with battery-like capacity, *RSC Adv.* 2 (2012) 12144. doi:10.1039/c2ra22265e.
- [15] W. Shimizu, S. Makino, K. Takahashi, N. Imanishi, W. Sugimoto, Development of a 4.2 V aqueous hybrid electrochemical capacitor based on MnO₂ positive and protected Li negative electrodes, *J. Power Sources* 241 (2013) 572–577. doi:10.1016/j.jpowsour.2013.05.003.
- [16] S. Makino, T. Ban, W. Sugimoto, Electrochemical Capacitor Behavior of RuO₂ Nanosheets in Buffered Solution and Its Application to Hybrid Capacitor, *Electrochemistry* 81 (2013) 795–797. doi:10.5796/electrochemistry.81.795.
- [17] S. Chou, Y.-X. Wang, J. Xu, J. Wang, H. Liu, S. Dou, A hybrid electrolyte energy storage device with high energy and long life using lithium anode and MnO₂ nanoflake cathode, *Electrochem. Commun.* 31 (2013) 35–38. doi:10.1016/j.elecom.2013.03.003.
- [18] K. Fukuda, T. Saida, J. Sato, M. Yonezawa, Y. Takasu, W. Sugimoto, Synthesis of Nanosheet Crystallites of Ruthenate with an α -NaFeO₂-Related Structure and Its Electrochemical Supercapacitor Property, *Inorg. Chem.* 49 (2010) 4391–4393.

doi:10.1021/ic100176d.

- [19] T. Zhang, N. Imanishi, S. Hasegawa, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, N. Sammes, LiPolymer Electrolyte/Water Stable Lithium-Conducting Glass Ceramics Composite for Lithium–Air Secondary Batteries with an Aqueous Electrolyte, *J. Electrochem. Soc.* 155 (2008) A965–A969. doi:10.1149/1.2990717.
- [20] T. Zhang, N. Imanishi, S. Hasegawa, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, N. Sammes, Water-Stable Lithium Anode with the Three-Layer Construction for Aqueous Lithium–Air Secondary Batteries, *Electrochem. Solid-State Lett.* 12 (2009) A132–A135. doi:10.1149/1.3125285.
- [21] T. Zhang, N. Imanishi, Y. Shimonishi, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, N. Sammes, Stability of a Water-Stable Lithium Metal Anode for a Lithium–Air Battery with Acetic Acid–Water Solutions, *J. Electrochem. Soc.* 157 (2010) A214–A218. doi:10.1149/1.3271103.
- [22] T. Zhang, N. Imanishi, Y. Shimonishi, A. Hirano, Y. Takeda, O. Yamamoto, N. Sammes, A novel high energy density rechargeable lithium/air battery, *Chem. Commun.* 46 (2010) 1661–1663. doi:10.1039/b920012f.
- [23] S. Liu, N. Imanishi, T. Zhang, A. Hirano, Y. Takeda, O. Yamamoto, J. Yang, Lithium Dendrite Formation in Li/Poly(ethylene oxide)–Lithium Bis(trifluoromethanesulfonyl)imide and N-Methyl-N-propylpiperidinium Bis(trifluoromethanesulfonyl)imide/Li Cells, *J. Electrochem. Soc.* 157 (2010) A1092. doi:10.1149/1.3473790.
- [24] S. Makino, T. Ban, W. Sugimoto, Towards Implantable Bio-Supercapacitors: Pseudocapacitance of Ruthenium Oxide Nanoparticles and Nanosheets in Acids, Buffered Solutions, and Bioelectrolytes, *J. Electrochem. Soc.* 162 (2015) A5001–A5006. doi:10.1149/2.0021505jes.

Figure captions:

Scheme 1. Schematic representation of the assembly of aqueous hybrid supercapacitor with multilayered Li_xC_6 negative electrode **after** Li^+ pre-doping process.

Fig. 1. Chronopotentiogram of graphite electrode during Li^+ pre-doping process in 1.0 M $\text{LiPF}_6/\text{EC-DEC}$ (1:1) at 0.05 C.

Fig. 2. Impedance spectra of Li (circles) and Li_xC_6 (triangles) | PEO-LiTFSI | LTAP | 1.0 M Li_2SO_4 | Pt at 60°C and the equivalent circuit used to fit the experimental data.

Fig. 3. Charge/discharge curves at (A) 0.102 and (B) 1.53 mA cm^{-2} for Li_xC_6 (solid line) and Li (dashed line) | PEO-LiTFSI | LTAP | 1.0 M Li_2SO_4 | AC at 60°C. Left axis: cell voltage in two-electrode configuration (black). Right axis: potential of AC positive electrode (red) and Li_xC_6 and Li negative electrode (blue).

Fig. 4. Impedance spectra of Li_xC_6 | PEO-LiTFSI-PP13TFSI | LTAP (circles) and Li | PEO-LiTFSI | LTAP | 1.0 M Li_2SO_4 | Pt (triangles) at 25°C.

Fig. 5. Charge/discharge curves of Li_xC_6 | PEO-LiTFSI-PP13TFSI | LTAP | 1.0 M Li_2SO_4 | AC at 0.102 mA cm^{-2} at 25°C. Solid line: 1st and 2nd cycles. Dashed line: 2999th and 3000th cycles. Left axis: cell voltage in two-electrode configuration (black). Right axis: potential of AC positive electrode (red) and Li_xC_6 negative electrode (blue).

Fig. 6. The specific capacity and the retention ratio as a function of cycles for Li_xC_6 | PEO-LiTFSI-PP13TFSI | LTAP | 1.0 M Li_2SO_4 | AC at 0.102 mA cm^{-2} at 25°C during long-term test.

Fig. 7. Charge/discharge curve at 0.036 mA cm^{-2} for Li_xC_6 | PEO-LiTFSI-PP13TFSI | LTAP | 2.0 M AcOH-AcOLi | RuO_2 nanosheet at 25°C . Left axis: Cell voltage in two-electrode configuration (black). Right axis: potential of RuO_2 nanosheet positive electrode (red) and Li_xC_6 negative electrode (blue).