

Supercapacitor-battery hybrid energy storage devices from an aqueous nitroxide radical active material

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A hybrid electrochemical energy storage device was fabricated in aqueous NaOH with the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) nitroxide radical as the active material, hydroquinone as the counter electrode active material, and an OH⁻-selective separating membrane. The working principle of this device was investigated and it can be considered as a supercapacitor-battery hybrid energy storage system. Device performance was characterized by cyclic voltammetry and galvanostatic charge-discharge testing. When using multi-walled carbon nanotubes (MWCNTs) as electrode support materials, a high pseudo-capacitance of 1280 F g⁻¹ was obtained with the TEMPO nitroxide radical as the active material at a 1 mV s⁻¹ scan rate. This was ~33 times larger than the inherent double layer capacitance of MWCNTs. The electrode material and active material dissolved in solution could potentially be substituted with similar materials. This simple design provides a new approach for fabricating high performance supercapacitor-battery hybrid energy storage devices.

nitroxide radical, electrochemical energy storage device, hybrid system, reversible redox reaction, aqueous solution electrolyte

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The demand for advanced electrochemical energy storage devices with increased power and energy densities is continuously increasing because of sustainable energy and environmental issues [1,2]. Supercapacitors represent the state of the art in high power systems, while rechargeable batteries (particularly lithium-ion batteries) are the highest energy storage facilities [3–5]. Hybrid energy storage devices, using both supercapacitor and battery electrodes in a single unit cell, provide a clever solution combining the advantages of the two energy storage systems. Clearly, such high performance hybrid devices cannot necessarily be achieved by combining any supercapacitor and rechargeable battery. Supercapacitors and rechargeable batteries operate over different potential ranges and in different electrolytes

[6,7]. Energy storage in traditional supercapacitors and rechargeable batteries is usually based on active solid electrode materials which limit energy density. If active materials with reversible redox properties can be stored in solution, high energy devices may be obtainable. The Li-Cu battery is an example of this, where a Cu-cathode in aqueous electrolyte and a Li-anode in non-aqueous electrolyte, are separated by a lithium super-ionic conductor glass film (LISICON) in the hybrid electrolyte [8]. The redox flow battery (RFB) has recently also received much attention because of its high-efficiency, low cost, large-scale energy storage where active materials are dissolved in electrolyte solution. The vanadium redox flow battery is thought to be the most practical candidate [9]. Present RFBs are based on inorganic active materials restricted by limited mineral resources. Organic active materials are good candidates for energy storage devices, because they can be synthesized from biomass

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via green chemistry and are more easily recyclable [10]. The 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) nitroxide radical is a stable organic species which undergoes reversible reduction and oxidation. Poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) containing embedded TEMPO has been applied to both cathodic active materials in rechargeable batteries and positive electrode materials in hybrid electrochemical capacitors [11]. In the current study, we report a hybrid electrochemical energy storage device using multi-walled carbon nanotubes (MWCNTs) as the supporting electrode, where all active materials dissolved in aqueous solution. An important point is the use of the TEMPO nitroxide radical as the anodic active material and hydroquinone (HQ) as the cathodic active material, which were separated by an OH^- -selective membrane. The device electrochemical performance was investigated by cyclic voltammetry and galvanostatic charge-discharge testing. The device afforded high capacitance through non-faradic reactions of supporting electrode via charge separation on the electrode material/electrolyte interfaces, and the faradic redox-reactions of TEMPO nitroxide radical between its different oxidation states [12]. While the former provides the well-known double layer capacitance, the latter results in high pseudocapacitance.

1 Materials and methods

The hybrid electrochemical energy storage device contained an anode and cathode separated by an OH^- -selective membrane (Astom Corp, Japan.), as shown in Figure 1(a). The

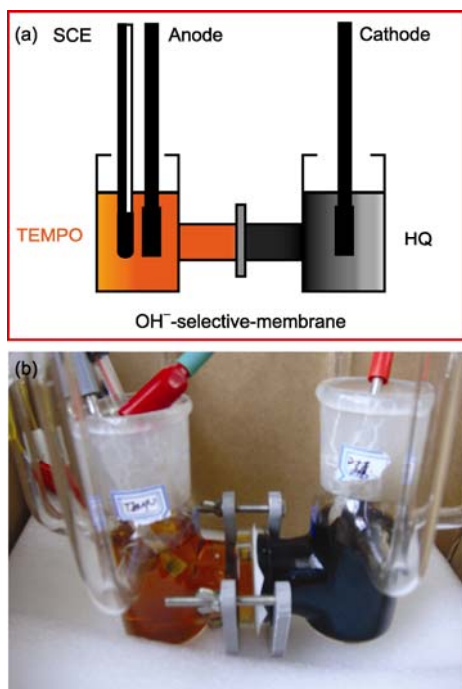


Figure 1 The hybrid electrochemical energy storage device prepared in this study: (a) schematic and (b) photograph.

membrane permitted solely OH^- to permeate it. A mixture of MWCNTs, carbon black and Teflonized acetylene black (TAB) at a weight ratio of 80:10:10, was pasted onto a Ni net ($4\text{ cm} \times 0.8\text{ cm} \times 0.1\text{ mm}$) which formed the two supporting electrodes. The active powder ($\sim 1.5\text{ mg}$) was pressed onto the Ni net and formed a pellet with $0.6\text{ cm} \times 0.6\text{ cm} \times 0.1\text{ mm}$ in length \times width \times thickness. Equimolar ratios of TEMPO nitroxide radical and HQ were dissolved in 100 mL of aqueous 1 mol/L NaOH as the active materials for the anode and cathode, respectively. Figure 1(a) shows that both the anode (working electrode) and reference electrode (saturated calomel electrode, SCE) were immersed in TEMPO/NaOH solution, while the cathode (counter electrode) was so in HQ/NaOH solution. Figure 1(b) shows an optical image of a real device built in this study.

Cyclic voltammograms (CVs) were measured on a Parstat 2273 advanced electrochemical system, at scan rates varying from 1 to 100 mV s^{-1} . Galvanostatic charge-discharge tests of the assembled device were carried out on an Arbin BT2000 system, over the voltage range $-0.8-0\text{ V}$ with respect to SCE under different current densities. All potentials reported were referenced to SCE.

2 Results and discussion

Figure 2(a) shows CV curves of the MWCNT electrode (line i), 5 mmol/L TEMPO nitroxide radical (line ii) and 5 mmol/L HQ (line iii), in 1 mol/L NaOH solution at a scan rate of 10 mV s^{-1} and $-0.8-0\text{ V}$ voltage window. The CV curve for MWCNT exhibited a nearly rectangular shape without obvious peaks, which is typical for capacitive behavior. The CV curve for TEMPO nitroxide radical exhibited a reversible redox peak at -0.4 V in NaOH solution, which was ascribed to the transition between the aminoxy anion state and the nitroxide radical state (Figure 3). This may have resulted in the redox capacitance. The difference between anodic (E_a : -393 mV) and cathodic (E_c : -436 mV) peak potentials was as small as 43 mV at a 10-mV s^{-1} scan rate, which implied a fast reversible electrochemical reaction for the TEMPO nitroxide radical. The CV curve for HQ exhibited two redox pairs at around -0.6 and -0.18 V , the former (E_a : -633 mV ; E_c : -604 mV) reflecting the reversible inter-conversion of HQ and 1,4-benzoquinone ($E_c-E_a = 29\text{ mV}$) (Figure 3). The peak current of the redox peak at -0.18 V decreased with increasing scan rate (not shown), which might not be used for supercapacitors due to the irreversible redox reaction. The device open circuit voltage was -0.16 V , and the initial cathodic peak represented the reduction of the TEMPO nitroxide radical to the aminoxy anion. HQ was correspondingly oxidized to 1,4-benzoquinone in aqueous NaOH. Cycling tests in Figure 2(b) showed no-obvious peak current loss after 90 cycles in 10 mmol/L TEMPO nitroxide radical, further demonstrating the excellent

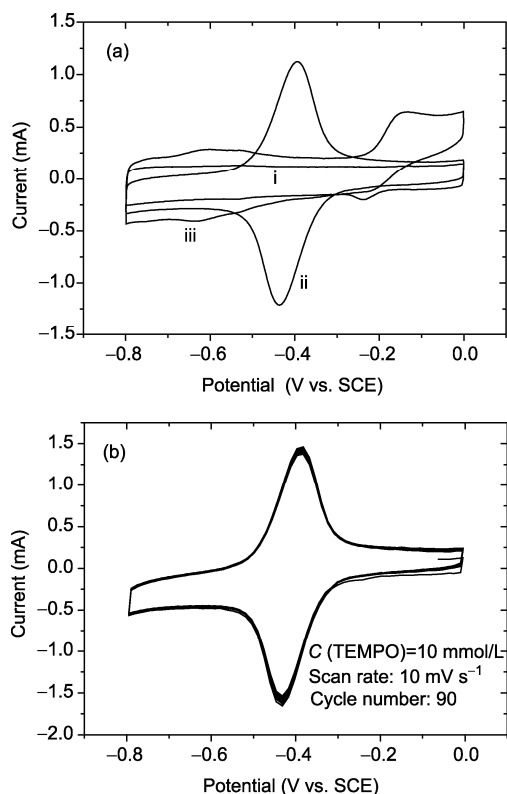


Figure 2 (a) CV curves of the MWCNT electrode in 0 mmol/L TEMPO nitroxide radical (i), 5 mmol/L TEMPO (ii) and 5 mmol/L HQ (iii), in 1 mol/L NaOH solution with a 10 mV s^{-1} scan rate. (b) CV curves in 10 mmol/L TEMPO nitroxide radical with a 10 mV s^{-1} scan rate.

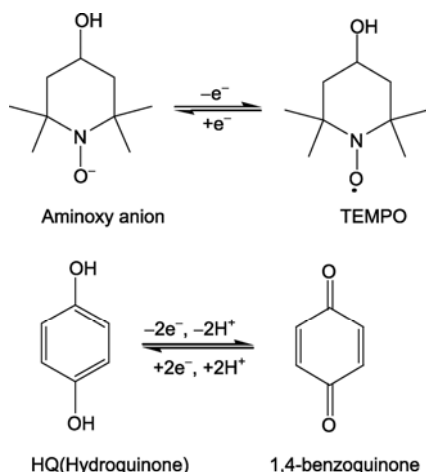


Figure 3 Reversible redox reactions of TEMPO nitroxide radical and HQ.

chemical stability of this redox system.

The specific capacitance was calculated from the CV curves using the equation $C = Q/mV$, where Q is the integration of current and time, V is the voltage range, and m is the mass of the MWCNT electrode. Specific capacitances for 1 mol/L NaOH electrolyte containing TEMPO nitroxide radicals at different concentrations are summarized in Figure 4 (a). Scan rates of 1, 2, 5, 10, 20, 50 and 100 mV s^{-1}

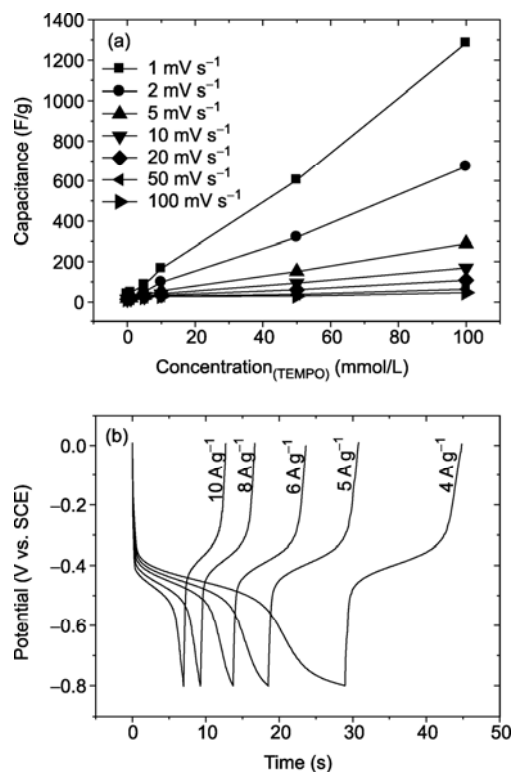


Figure 4 (a) Specific capacitance of the MWCNT electrode with increasing TEMPO nitroxide radical concentration, in 1 mol/L NaOH electrolyte at different scan rates. (b) Galvanostatic charging-discharging curves in 100 mmol/L TEMPO nitroxide radical at different current densities of 10, 8, 6, 5 and 4 A g^{-1} .

were performed for each TEMPO nitroxide radical concentration. Figure 4(a) indicates that specific capacitance increased with increasing radical concentration and decreased with increasing scan rate. A greater quantity of TEMPO nitroxide radicals undergoing redox reaction may have been responsible for the former trend. The latter may have been attributed to less efficient diffusion of TEMPO nitroxide radicals to the MWCNT electrode reaction interface [13]. For a TEMPO nitroxide radical concentration of 100 mmol/L, capacitance exceeded 1200 F g^{-1} when it was only 38 F g^{-1} in the absence of TEMPO nitroxide radical at a 1-mV s^{-1} scan rate. Thus, high pseudo-capacitance was contributed to by the TEMPO nitroxide radical redox reaction in aqueous NaOH.

Galvanostatic charge/discharge measurements were carried out to further investigate the electrochemical performance of the device. A potential range $-0.8\text{--}0 \text{ V}$ at different current densities were used for the tests, which were carried out in 100 mmol/L TEMPO nitroxide radical and 1 mol/L NaOH solution. Figure 4 (b) shows the measurement was conducted by first discharging and then charging the device. Curves were comprised of three distinct parts: two sharp voltage drops from 0 to -0.3 V and from -0.6 to -0.8 V , and one voltage plateau from -0.3 to -0.6 V . The two voltage drops may have been ascribed to the electric double-

layer capacitance of the MWCNTs electrode, while the long plateau may have been caused by the combination of the electric double-layer capacitance from MWCNTs and the faradaic capacitance from the TEMPO nitroxide radical [14]. There was a discharging-charging voltage platform at -0.4 V, which was consistent with the redox peak at -0.4 V observed for TEMPO nitroxide radical reaction. Discharge time increased with decreasing current density, hence capacitance increased. These results are in good agreement with those from the above CV curves.

3 Conclusions

A novel environmental-friendly hybrid energy storage device has been developed, with the TEMPO nitroxide radical serving as the active material, HQ as the counter active material and an OH^- -selective separating membrane. The reversible redox reaction of the TEMPO nitroxide radical provided a significant pseudo-capacitance far beyond the electric double-layer capacitance of MWCNTs. The specific capacitance increased with increasing TEMPO nitroxide radical concentration. A maximum specific capacitance of 1200 F g^{-1} was obtained at the scan rate of 1 mV s^{-1} . The electrode material and active material dissolved in solution could potentially be exchanged for alternative materials, with either high electric double-layer capacitance or high pseudo-capacitance within the appropriate electrochemical potential ranges. This simple design provides a new approach for fabricating high performance supercapacitor-battery hybrid energy storage devices.

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- 1 Arico A S, Bruce P, Scrosati B, et al. Nanostructured materials for advanced energy conversion and storage devices. *Nat Mater*, 2005, 4: 366–377
- 2 Armand M, Tarascon J M. Building better batteries. *Nature*, 2008, 451: 652–657
- 3 Guo Y G, Hu J S, Wan L J. Nanostructured materials for electrochemical energy conversion and storage devices. *Adv Mater*, 2008, 20: 2878–2887
- 4 Li H, Wang Z X, Chen L Q, et al. Research on advanced materials for Li-ion batteries. *Adv Mater*, 2009, 21: 4593–4607
- 5 Yan J, Wei T, Fan Z, et al. Preparation of graphene nanosheet/carbon nanotube/polyaniline composite as electrode material for supercapacitors. *J Power Sources*, 2010, 195: 3041–3045
- 6 Li H Q, Wang Y G, Na H T, et al. Rechargeable Ni-Li battery integrated aqueous/nonaqueous system. *J Am Chem Soc*, 2009, 131: 15098–15099
- 7 Li H Q, Wang Y G, He P, et al. A novel rechargeable Li-AgO battery with hybrid electrolytes. *Chem Comm*, 2010, 46: 2055–2057
- 8 Wang Y G, Zhou H S. A new type rechargeable lithium battery based on a Cu-cathode. *Electrochem Commun*, 2009, 11: 1834–1837
- 9 Skyllas-Kazacos M, Kazacos G, Poon G, et al. Recent advances with UNSW vanadium-based redox flow batteries. *Int J Energy Res*, 2010, 34: 182–189
- 10 Liao C, Wei Z D, Chen S G, et al. Synergistic effect of polyaniline-modified Pd/C catalysts on formic acid oxidation in a weak acid medium (NH)SO. *J Phys Chem C*, 2009, 113: 5705–5710
- 11 Li H Q, Zou Y, Xia Y Y. A study of nitroxide polyradical/activated carbon composite as the positive electrode material for electrochemical hybrid capacitor. *Electrochim Acta*, 2007, 52: 2153–2157
- 12 Nishide H, Iwasa S, Pu Y J, et al. Organic radical battery: Nitroxide polymers as a cathode-active material. *Electrochim Acta*, 2004, 50: 827–831
- 13 Maier J. Nanoionics: Ion transport and electrochemical storage in confined systems. *Nat Mater*, 2005, 4: 805–815
- 14 Yan J, Wei T, Shao B, et al. Preparation of a graphene nanosheet/polyaniline composite with high specific capacitance. *Carbon*, 2010, 48: 487–493

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