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Full Length Article

Understanding and controlling the rest potential of carbon nanotube-based supercapacitors for energy density enhancement

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ABSTRACT

We present a novel method for enhancing the energy density of an electrical double layer capacitor (EDLC). Surface modification of single-walled carbon nanotube (SWNT) electrodes significantly affects the rest potential (E_0) of EDLCs; acid treatment and polyethyleneimine (PEI) coating of SWNTs shift E_0 toward more positive and more negative values, respectively. Adjusting E_0 towards the center of the electrolyte stability window can increase the cell voltage and hence the energy density. PEI coating on SWNTs increases the cell voltage from 0.8 V to 1.7 V in tetrabutylammonium perchlorate (TBAP)/tetrahydrofuran (THF) electrolyte, and from 2.5 V to 3.1 V in tetraethylammonium tetrafluoroborate ($TEABF_4$)/3-cyanopropionic acid methyl ester (CPAME), respectively. Moreover, PEI-SWNT EDLCs exhibit excellent cycling stability (92% of capacitance retention over 10000 cycles). We attribute the shift in E_0 to a change in the Fermi level of SWNTs owing to the surface charge modification. Injection of electrical charge into PEI-SWNTs consistently yielded similar trends and thus validated our hypothesis. Our results may help to push various electrolytes that have been overlooked so far to new frontiers for obtaining high energy-density supercapacitors.

1. Introduction

It is important to devise and explore new ways to improve the performance of energy storage devices to meet the ever-increasing energy demands of society. Supercapacitors are promising energy storage systems with high power density, fast charge-discharge dynamics, and long cycle lifetime. These characteristics make supercapacitors suitable for broad range of applications, such as grid power buffers, harvested energy storage devices, energy recovery devices, hybrid electrical vehicles, uninterruptible power supply sources, and memory backup devices [1,2]. Although supercapacitors exhibit higher energy density than conventional capacitors, the energy density of a typical supercapacitor is lower than that of other energy storage devices, such as batteries [3,4]. Therefore, it is highly desirable to improve the energy density characteristic of supercapacitors while maintaining their advantageous power performance.

Researchers have developed various strategies to enhance the energy density of supercapacitors by incorporating redox materials and/or using asymmetric electrode configurations [5–8]. For example, metal oxides and conductive polymers can be used as pseudo-capacitive materials to significantly improve capacitance. Recently, it has been demonstrated that incorporation of redox molecules such as hydroquinone and decamethylferrocene into electrolytes can improve the capacitance and/or the cell voltage of capacitors [9,10]. Combining supercapacitor-type and battery-type electrodes can also improve the energy density of supercapacitors. Since all of the above-mentioned supercapacitors involve redox chemical reactions, enhancement of their energy density could be accompanied by a certain reduction in their power performance.

One interesting and promising approach would be to improve the energy density of EDLCs without the involvement of redox chemical reactions. This is because EDLCs are generally faster than pseudo-capacitors, because the operation of EDLCs is based on facile physical adsorption and desorption of ions rather than on redox chemical reactions. We posit that properly adjusting the rest potential (E_0) of EDLCs should increase their cell voltage and thus the energy density. The rest potential E_0 is defined as the potential at which the positive and negative electrodes are placed relative to the reference electrode when the cell voltage is 0 V. The value of E_0 significantly affects the characteristics of EDLCs [11,12]. When positive and negative electrodes contain equal amounts of active material, the potentials of two electrodes will symmetrically deviate from E_0 during charging. If E_0 is located away from the center of

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