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Trade-off between capacitance and cycling at elevated temperatures in redox additive aqueous electrolyte based high performance asymmetric supercapacitors

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ABSTRACT

High surface area mesoporous MWCNTs/ZrO_2 and MWCNTs/WO_3 composites are used to fabricate asymmetric supercapacitors (ASCs) in 1 M Li_2SO_4 aqueous electrolyte with and without addition of KI. The addition of redox electrolyte additive leads to simultaneous enhancement in specific energy and power. These ASCs, when operated upto temperatures $\leq$60 °C, show reasonably stable specific capacitance and cycling stability. It is observed that the temperature predominantly affects the capacitance fade during galvanostatic charging-discharging whereas specific capacitance actually increases slightly at elevated temperatures. The Gouy-Chapman theory fails to explain such improvements in the specific capacitance. The improvement is strongly governed by the activation energy associated with the diffusion of ionic species and their chemical potential. Further, the capacitance fade at higher temperatures can be attributed to: (a) the total "time spent" at a given temperature during cycling and (b) reduced kinetic barrier for iodine/iodide redox pairs at the positive electrode/electrolyte interface, which facilitates H_2 generation at the negative electrode and induce charge-imbalanced state.

1. Introduction

There is growing need for simultaneously enhancing the specific energy and power of supercapacitors (SCs). This will make possible their application in the rapidly growing market of wearable and portable electronics [1–4]. Lightweight, thin or even flexible supercapacitors with high durability, cycle life, wide voltage and temperature window of operation are therefore becoming essential. Most activities are being focused on the development of next generation electrode materials with tunable porosity, surface area, conductivity, thermal and mechanical stability [5,6]. This has mostly led to the improvement in either specific power or energy values near room temperature [7,8]. It is now clear that more effort has to be put-in to look into supercapacitor configurations, electrolytes and separators to achieve supercapacitors for attractive applications mentioned above. This paper proposes a synergetic strategy of using redox additive electrolyte for simultaneously improving the specific power and energy values in asymmetric supercapacitors and also ensure desirable temperature window of operation [9,10].

Fabricating high performance supercapacitors, which are also stable at elevated temperatures, is a non-trivial exercise [11,12]. It is known that, at higher temperatures, factors such as ion conductivity of electrolytes, solubility limits, viscosity variation, thermal stability, etc. become important. Most of these factors, if not properly controlled, can lead to severe degradation in the device performance [13]. Supercapacitor performance at slightly elevated temperatures is also critical for automotive industries as the surrounding temperature is bound to increase when the engine is operational [14]. Strangely, over the last few years, there are very few studies dealing with the temperature effects on the electrochemical performance of aqueous SCs [15,16].

The high performance asymmetric supercapacitor discussed in this paper was fabricated using MWCNTs/ZrO_2 (MWZ; positive electrode) and MWCNTs/WO_3 (MWW; negative electrode) in 1 M Li_2SO_4 aqueous electrolyte with optimized concentration of redox additive. The properly charge balanced ASCs lead to simultaneous increase in the specific power and energy values. The use of carefully chosen transition metal oxides, with large difference in their work functions, for use at negative and positive electrodes, allows the device to work in a wide voltage window. At room temperature (RT), ASCs showed stable operation up to 2.2 V with high coulombic efficiency (~94%). The use of redox electrolyte additive viz., KI, causes increase in the active species due to the

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oxidation/reduction reactions which occur at the electrode/electrolyte interface due to the iodide/iodine redox reactions. If the porosity of the electrode materials is suitably tuned, the solvated iodine species (such as polyiodides) of size ~1.8 nm can also intercalate and accumulate inside the surface. This can lead to significant enhancement in charge storage, resulting in specific power and energy enhancement.

Our novel ASCs (with addition of KI) delivered specific energy as high as ~133 Wh kg^{-1} with capacitance fade of only 10% over 1000 charge-discharge operations. As emphasized earlier, the temperature dependent performance of supercapacitors is critical. The performance of our supercapacitors, at elevated temperatures, is also presented in the paper. Actually, slight increase in the capacitance value is observed at higher temperatures. The ASCs fabricated using redox additive aqueous electrolyte can operate nicely up to 60 °C without significant performance loss. Above this temperature, loss in performance was discernible. The reasons for these observations are also explained in detail.

2. Experimental

The synthesis and physical characterizations of MWZ and MWW composites are given in the supporting evidence (ESI Fig. S1-S3). The MWZ composite comprised of nano-sized ZrO_2 and MWCNTs whereas MWW composite contained inter-twinned WO_3 nanoplates and MWCNTs (see ESI Fig. S3).

For the fabrication of ASC devices, Whatman glass microfiber filters gf/c was used as separator sandwiched between two electrodes with dimension 1 cm × 1 cm in CR2032 type coin cell. For three electrode measurements, the electrodes were immersed in 100 ml pyrex glass beaker provided by Metrohm Autolab. As for temperature dependent study, the coin cell was kept in PID controlled stainless steel lined cylindrical oven. To avoid discrepancy, the coin cell was kept near the thermocouple of the oven during each temperature set measurement. About 1 h were given to coin cell for attaining thermal equilibrium at each temperature set. The temperature variation around the fixed temperature was $\Delta T = \pm 1\,^{\circ}C$.

A concentration of 7.5 mmol for redox additive (KI) was deduced as an optimal to improve overall performance of ASCs. Therefore, ASCs were fabricated using such mesopores MWZ (positive) and MWW (negative) electrode materials in three electrolyte systems i.e., 1 M Li_2SO_4, 1 M Li_2SO_4 + 7.5 mmol KI and 1 M Li_2SO_4 + 15 mmol KI (to ensure that no improvement is obtained at higher redox additive concentration) and tested at elevated temperatures. The fabricated ASCs were tested by

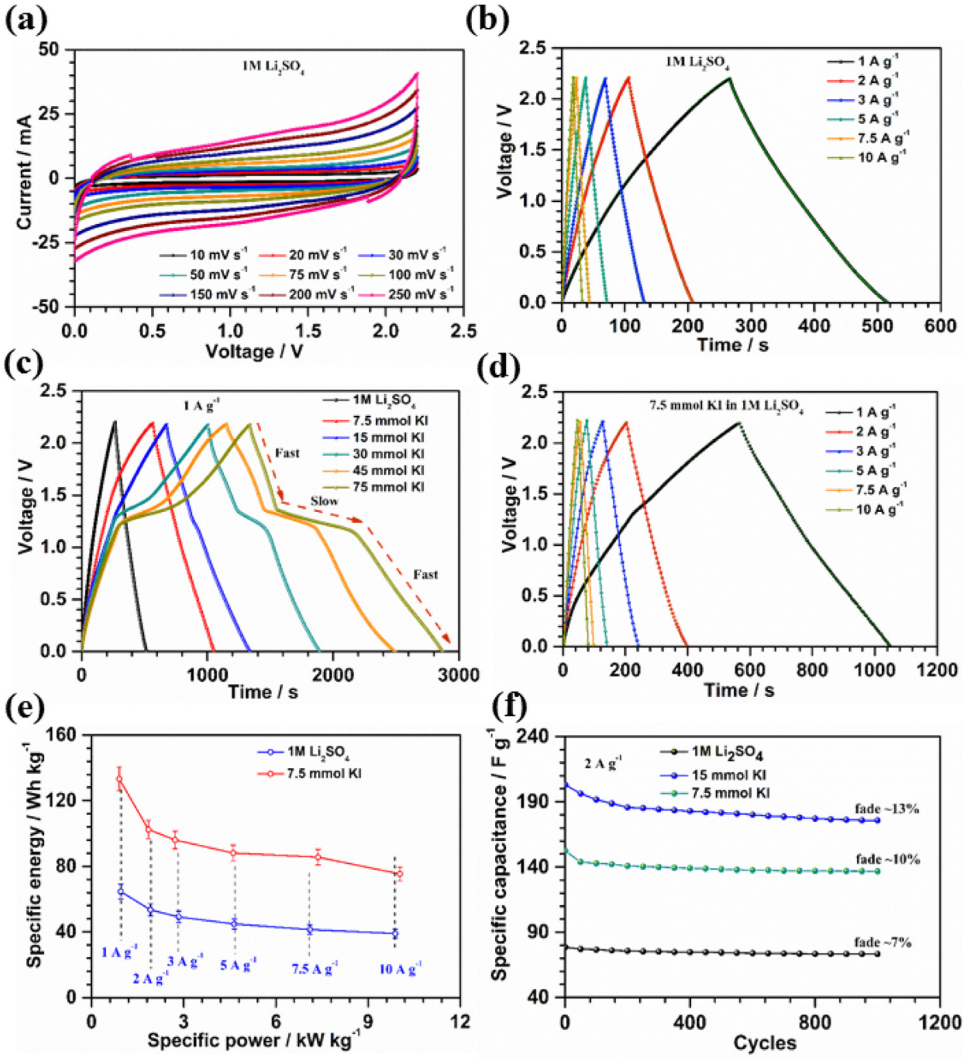

Fig. 1. (a-b) Two electrode CVs and charge-discharge curves for the ASCs in 1 M Li_2SO_4 aqueous electrolyte; (c) charge-discharge curves at 1 A g^{-1} for the ASCs with and without KI addition; (d) charge discharge curves for the ASCs assembled with addition of 7.5 mmol KI; (e) Ragone plot for the ASCs with and without addition of KI and (f) cycling stability test for the ASCs.