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Study on effects of applied current and voltage on the ageing of supercapacitors

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ABSTRACT

To investigate the degradation mechanism of supercapacitors from world-famous commercial manufacture Nesscap at different failure-mode, post-mortem pore structure and chemical ageing analyses were applied for the positive and negative electrodes components, followed by the ageing behavior characterization during galvanostatic charge/discharge (GCD) cycling at room temperature for 60,000 cycles. From the test results, it can be observed that the supercapacitors were damaged to some extent at higher currents (>4 A), while the devices were destroyed at excess voltage (>3.2 V). The main reason in chemical composition for the difference was that a large amount of binder disappeared from the aged electrodes at higher voltage and there was a passivation film formed on the surface of the collector, while slight variation existed in the electrode materials of the aged supercapacitors at higher current. The components deterioration further damaged the unity of the electrodes and caused the increase of the resistance and the decrease of the capacity.

1. Introduction

Electrochemical double-layer capacitors store electrical energy mainly in an electrostatic way on the interface between a solid electrode and an electrolyte [1], and are commonly known as ultracapacitors, supercapacitors or electrochemical supercapacitors. Supercapacitors show great advantages in fast charge/discharge rates (in seconds), high specific power (up to 10 kW kg^{-1}) and almost unlimited cyclability (500,000–1,000,000 cycles) [2,3]. In addition, supercapacitors have long shelf time and service life (more than 10 years [4]). Supercapacitors and supercapacitor modules have attracted considerable attention in many fields, including line-filtering, portable power supplies, hybrid vehicles, wind turbine systems and photovoltaic systems [2,5–7].

The lifetime and reliability are important for supercapacitors as a significant component in storage systems. Taking into account the reliability and safety of a supercapacitor, especially for a supercapacitor module, it is rather necessary to investigate the aging behavior of the supercapacitor and especially the ageing and degradation mechanisms. Many works [8–16] have been studied on the influence of overvoltage and extended temperature on the degradation of supercapacitors. According to Arrhenius theory, the life of the supercapacitors will be reduced by half for a temperature increase of 10 °C or a voltage increase of 0.1 V, when the effective activation energy was about −0.57 eV (54 kJ mol^{-1}) between 0 °C and 60 °C [8]. Ruch et al. [10] investigated the ageing of supercapacitors consisting of activated carbon electrodes and acetonitrile electrolyte through increasing constant voltages, and found that the pores of aged positive electrodes suffered a severe blockage.

However, we noticed that the cycling lifetime of supercapacitors was also affected by charge-discharge current during constant current cycling. This made us think that current may be another factor for acceleration of ageing of supercapacitors. In addition, P. Kreczanik et al. [11] also confirmed the influence of effective current on ageing and lifetime of supercapacitors. What is more, the supercapacitor is usually charged/discharged at a high current density to achieve higher power density as a start and stop system of micro-hybrid vehicle (MHEV), hybrid electric vehicle (HEV) or hybrid fuel-cell vehicle (HFCV). Sometimes the supercapacitors need work at a high working voltage to realize an emergency power supply with higher energy density and excellent reliability. One of the objectives of this study is to research on the performance behavior of the supercapacitors under very aggressive conditions of applied current and voltage. Another objective is to try to

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investigate how the differences are impacted by applied current and voltage.

In this paper, we seek to investigate the cycling ageing of a kind of world-famous commercial supercapacitors (Nesscap, 2.7 V/10 F). We adapted conventional galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy to investigate the evolution of supercapacitors' performances with time of cycling, eg. cycle efficiency and electrochemical impedance, under different operation conditions. The detail post-mortem analyses of the aged supercapacitors contributed to explore the degradation process. This work addresses the different influences of charge/discharge applied current and cell voltage and the intrinsic reasons for that difference.

2. Experimental

2.1. Supercapacitors and their ageing process

Electrochemical ageing was performed with cylindrical commercial supercapacitors at constant current charge-discharge cycling. The detailed descriptions of the supercapacitors are shown in Table 1. The group of supercapacitors have a nominal capacity of 10 F and a rated voltage of 2.7 V, consisting of activated carbon based electrodes and acetonitrile based electrolyte. Cycling ageing was controlled by the medium machine of the battery test system (BTS) Neware 4008 (Shenzhen Neware Co., Ltd, China). GCD was carried out under room constant temperature (at about 25 °C) without cooling or heating. The cycling setup in detail and the corresponding ageing conditions are shown as Tables 2 and 3.

Electrochemical impedance was measured with Bio-logic VMP3 under open circuit conditions. The frequency range is between 100 kHz and 10 mHz.

2.2. Post-mortem analyses of the aged electrodes

The fresh supercapacitor, the aged supercapacitor at 6 A and the damaged supercapacitor at 3.5 V were disassembled in an argon-filled glove box and rinsed with acetonitrile for 24 h to remove residual electrolyte, and then they were dried and stored in a desiccator before further analysis.

The morphology microstructure of the electrodes was characterized by scanning electron microscopy (SEM, Nova NanoSEM 450, FEI Co. USA). Pore structure was characterized by nitrogen adsorption/desorption method at 77 K at various equilibrium pressure values with a porosimeter (Quantachrome Co., USA). The specific surface area (SSA) of the samples was calculated with five-point Brunauer-Emmett-Teller (BET) in the range of $P/P_0 = 0.01–0.1$. The pore distributions of the electrodes materials were calculated by nonlocal density functional theory (NLDFT) equilibrium model.

In order to analyse the side reaction, the chemical compositions and their valence states were analysed by X-ray photoelectron spectra (XPS, 250Xl, Thermo Fisher Co.). The survey spectra (1350 eV to −10 eV) were recorded with a pass energy of 80 eV, while the fine spectral scans for O1s and C1s were recorded with a pass energy of 20 eV. Infrared spectra were collected on an attenuated total reflectance (ATR) unit in an Equinox 55 infrared spectrometer (Bruker, Germany). All spectra were referenced to the raw spectrum of air. Using the thermogravimetry-differential scanning calorimetry (TG-DSC) integrated analyzer (STA449 F3, NETZSCH, Germany), we investigated the positive and negative materials stripped from the aged and new supercapacitors, respectively.

3. Results and discussion

3.1. Ageing at different currents and voltages

Ageing of supercapacitors is embodied in many aspects, including capacity fade, resistance growth, leak current growth and self-discharge aggravation, etc. The definition of the supercapacitors end of life usually depends on their manufacturer. In general, the limit is set to 20% loss of the nominal capacitance or more than 100% growth of the equivalent series resistance [17].

Fig. 1 exhibits the evolution of capacitance, resistance and GCD curves with applied currents. The capacitance retention decreased with the increase of cycle number from 1 to 60,000 cycles and a larger capacitance retention loss occurred in the supercapacitors aged at applied current higher than 4 A (Fig. 1a). For equivalent series resistance, there seemed to be no regular change tendency, while the increase was concentrated in 10%–30% (Fig. 1b, the inset). At 1 A and 6 A the supercapacitors had the biggest diffusion resistance (Fig. 1b), may because that the applied current played a leading role in the ageing of the supercapacitors at above 4 A, while ageing time played a leading role when below the usable continuous current 3.4 A (Supporting information, Fig. S1). The shapes of GCD curves at various applied current were approximately linear, and the IR drop increased gradually with the increase of applied current (Fig. 1c). Fig. 1d further confirms that currents higher than 4 A may cause a dramatical loss to performance of supercapacitors.

Fig. 2 illustrates how the performance of the supercapacitors changes with voltage ranges. Operation voltage higher than the nominal voltage 2.7 V turn out to be a proper option to accelerate ageing. There was an identical shape among the impedance of supercapacitor at a cell voltage range less than 3.2 V while the curves show an obvious shift to the right with the increase of voltage, which indicated that the supercapacitors aged under a larger voltage arose an increase of equivalent series resistance and diffusion resistance (Fig. 2b, the inset). Furthermore, the appearance of semi-circle in the spectra of the supercapacitor at 3.5 V indicated a deterioration in the contact among activated carbon particles or between active materials and current collector. The voltage profiles at the 60,000th cycle are shown in Fig. 2c, where the maximum voltage was varied from 2.7 V to 3.5 V. The shape of the curves deviated clearly from the curve at 2.7 V for charging at higher voltage, especially voltage higher than 3.2 V. Comparing Figs. 1d and 2d, it can be seen that the supercapacitors aged under high voltages (<3.2 V) had higher final capacitance. However, capacitance of supercapacitors decreased dramatically if working for longer time or under higher voltages.

3.2. The pore structure ageing of the electrode materials

The capacitance of the supercapacitor depends on the SSA of the electrode materials and pore size distribution. Generally, larger SSA and the proportion of pores with a diameter of 0.7–1 nm (the size of BF_4^- and TEA^+ is around 0.3 nm and 0.7 nm [18,19]) and 2–5 nm

Table 1
Supercapacitors datasheet. Data from: NCE_2017_Datasheet_Nesscap ultracapacitors [online] http://www.nesscap.com/(accessed June 2017).

Rated Capacity	Rated Voltage	Surge Voltage	Initial Series Resistance (DC)	Maximum Cycle Life	Usable Continuous Current (ΔT = 15 °C)
10 F	2.7 V	2.85 V	20 mΩ	500,000 cycles	3.4 A