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Effects of Supercapacitor Physics on Its Charge Capacity

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Abstract

This paper investigates the effects of three aspects of the supercapacitor physics on its charge capacity: porous electrode structure, charge redistribution, and self-discharge. The relationship between the delivered charge and the discharge current is examined for both the upper and lower bounds of the utilized charge capacity, which refers to the amount of charge delivered during a constant current discharge process. In the upper bound case, Peukert's law applies when the discharge current is above a certain threshold and does not apply anymore if the discharge current is below the threshold. In the lower bound case, if the discharge current is above the threshold, the delivered charge increases when the discharge current decreases although the increase rate is lower compared to that in the upper bound case. The individual and combined effects of supercapacitor physics are studied. The porous electrode structure and the charge redistribution process result in an increase in the delivered charge when a smaller discharge current is applied. The impact of self-discharge is negligible when the discharge current is relatively large. If the discharge current is sufficiently small, self-discharge results in a significant energy loss and consequently a drop in the delivered charge.

Keywords

Supercapacitor; charge capacity; porous electrode structure; charge redistribution; self-discharge

I. Introduction

Among various energy storage technologies, supercapacitors are advantageous in several aspects such as high power density and long cycle life. Therefore, supercapacitor-based energy storage systems have been employed by a number of applications including electric and hybrid vehicles, smart grid, wireless sensor networks, and biomedical devices. Modeling and characterization of supercapacitors have been of great interest. Supercapacitors are usually constructed using porous carbon electrodes [1]. The porous electrode theory [2] suggests that an electrode can be modeled as an RC transmission line [3]. Consequently, a ladder circuit [4] composed of multiple RC branches with different time constants captures the distributed nature of the supercapacitor capacitance and resistance. To reduce the model complexity, different versions of simplified equivalent circuit models [5]–[8] have been proposed. In addition, various models have been developed to investigate a particular aspect of the supercapacitor behavior such as self-discharge [9]–[13], charge redistribution [14]–[16], voltage dependency of capacitance [14], [17], [18], as well as power and energy capabilities [19]–[22].

In addition to modeling and characterization, how to accurately and quickly estimate the supercapacitor state of charge (SOC) is also a critical research topic. Although the supercapacitor terminal voltage is a natural indicator of its state, accurate estimation of the state is still challenging because the supercapacitor capacitance and equivalent series resistance (ESR) are affected by multiple factors such as its terminal voltage [23], ambient temperature [24], and aging condition [25] in a complex manner. Numerous frameworks have been proposed to identify supercapacitor parameters and estimate supercapacitor states, which include offline methods based on electrochemical impedance spectroscopy (EIS) [26] or waveform relaxation [27] as well as online approaches utilizing Kalman filters [28], [29], recursive least squares [30], [31], or Lyapunov-based adaptation law [32].

Recently, the impact of supercapacitor physics especially the charge redistribution process on various aspects of the supercapacitor behavior has been investigated. Charge redistribution is a relaxation process originated from the porous electrode structure of supercapacitors. Due to the distributed nature of the supercapacitor capacitance and resistance, there is a potential distribution down the electrode pores when the electrode is charged or discharged [33], or equivalently, the pores at or near the surface of the electrode are accessed first followed by the pores at the bottom. Therefore, the charge stored in the supercapacitor tends to redistribute among different RC branches to reach an equilibrium. In addition to modeling and characterization of charge redistribution [14]–[16], various aspects of this process have been extensively investigated, which include its effects on the supercapacitor terminal voltage behavior [34]–[38], energy loss associated with this process [34], [39], and its impact on power management in wireless sensor networks [34], [40]–[42]. In particular, the impact of charge redistribution on the amount of charge delivered by a supercapacitor during one or multiple constant current discharge processes has been studied [43].

Based on the methodology developed in [43], this paper conducts a comprehensive and in-depth study of the effects of three aspects of the supercapacitor physics on its charge capacity: porous electrode structure (i.e., distributed nature of capacitance and resistance), charge redistribution, and self-discharge. Specifically, the upper and lower bounds of the utilized charge capacity (i.e., the amount of charge delivered during a constant current discharge process) and the total charge capacity (i.e., the total available charge stored in the supercapacitor) are examined. This paper extends [43] in three aspects: (1) the rated capacitance of the supercapacitor samples is expanded from 100 F only to three values: 10, 100, and 350 F; (2) the initial voltage of the constant current discharge experiment is swept and three other values (i.e., 2, 1.35, and 0.7 V) are considered in addition to the rated voltage of 2.7 V; and (3) the swept discharge current range is extended. These extensions lead to new results and observations, which are explained by the individual and combined effects of the three aspects of the supercapacitor physics. In particular, this paper reveals that the impact of self-discharge becomes significant when the discharge current is sufficiently small, which results in a drop in the utilized charge capacity.

The remainder of this paper is organized as follows. Section II studies the upper bound of the utilized charge capacity corresponding to a fully charged supercapacitor. Section III examines the lower bound of the utilized charge capacity associated with a partially charged

supercapacitor. Section IV compares the bounds of the utilized charge capacity. Section V compares the bounds of the total charge capacity. Section VI concludes this paper.

II. Upper Bound of Utilized Charge Capacity

A. Experiments and Results

This section investigates the upper bound of the utilized charge capacity of supercapacitors, which is measured by discharging a fully charged supercapacitor after a long time constant voltage charge process [43]. The experiments are designed and performed using the methodology developed in [43]. Specifically, the three supercapacitor samples with different rated capacitances from different manufacturers listed in Table I are tested using an automated Maccor Model 4304 testing system. In fact, sample 2 is also examined in [43].

For each sample, a set of constant current discharge experiments is performed when the initial voltage of the discharging process is fixed at a particular value. The rated voltage is the same for the three samples and the initial voltage is approximately linearly swept: 2.7, 2, 1.35, and 0.7 V. To illustrate the experiment design, Fig. 1 shows the measured supercapacitor terminal voltage during a 10 A experiment when the initial voltage is 2.7 V for sample 2. During this experiment, the supercapacitor is first conditioned by ten charging-redistribution-discharging cycles to minimize the effect of residual charge [44]. It is then charged by a constant voltage source of 2.7 V for 3 hours, which is designed to fully charge the supercapacitor. After that, a 10 A constant discharge current is applied and the supercapacitor is discharged to 0.01 V. The discharging termination voltage is set as 0.01 instead of 0 V for safety considerations. Taking 2.7 V as the initial voltage and 0.01 V as the cutoff voltage, the charge delivered during this constant current discharge process is calculated as

$$Q = It, \quad (1)$$

where I is the discharge current and t is the discharge time. For this experiment, the delivered charge is 252.4 C, which is referred to as the utilized charge capacity. In this paper, “delivered charge” means “utilized charge capacity” by default and these two terms are used interchangeably. The experiment continues to estimate the total charge capacity, which will be examined in Section V. After the supercapacitor voltage reaches the discharging termination condition of 0.01 V, the discharge current is disconnected and the supercapacitor experiences charge redistribution, which results in an increase in the terminal voltage. Once the terminal voltage increase rate is less than 0.01 V per 5 minutes, the charge redistribution process is considered complete and the discharge current is applied again. This discharging-redistribution cycle is repeated ten times to extract the charge stored in the supercapacitor to the maximum extent possible. For this experiment, the sum of the charge delivered during the ten discharging-redistribution cycles is 293.7 C, which is referred to as the total charge capacity.

Depending on the supercapacitor sample specifications and the supercapacitor tester capabilities, a set of constant discharge currents is swept for each sample. For sample 2, nine

currents are selected: 10, 5, 1, 0.5, 0.1, 0.05, 0.01, 0.005, and 0.0025 A. Fig. 2 shows the measured relationship between the delivered charge and the discharge current. The initial voltage is swept and the cutoff voltage is fixed at 0.01 V. For brevity, Figs. 3 and 4 only show the results for samples 1 and 3 when the initial voltage is 2.7 and 0.7 V, respectively. Compared to [43], this paper extends the supercapacitor charge capacity study in three aspects: (1) the rated capacitance of the supercapacitor samples is expanded from 100 F only to three values: 10, 100, and 350 F; (2) the initial voltage of the constant current discharge experiment is swept and three other values (i.e., 2, 1.35, and 0.7 V) are considered in addition to the rated voltage of 2.7 V; and (3) the swept discharge current range is extended (e.g., 0.005 and 0.0025 A are added for sample 2). These extensions lead to the following results and observations.

First, the relationship between the delivered charge and the discharge current is similar for all samples at all initial voltages. Specifically, the delivered charge pattern is partitioned into two pieces: Peukert's law applies when the discharge current is above a certain threshold and does not apply anymore when the discharge current is below the threshold. Originally developed for lead-acid batteries, Peukert's law [45] states that the delivered charge of a battery depends on the discharge current: the larger the discharge current, the less the delivered charge. Take Fig. 2(a) for instance. Clearly, for the seven discharge currents (i.e., 10, 5, 1, 0.5, 0.1, 0.05, and 0.01 A), the delivered charge increases when the discharge current decreases, which indicates that Peukert's law applies. For the other two discharge currents (i.e., 0.005 and 0.0025 A), however, the delivered charge decreases when the discharge current decreases and Peukert's law does not apply anymore. In fact, the delivered charge peaks at 0.01 A when the nine discharge currents are considered. This observation can be interpreted as follows. While Peukert's law applies when the discharge current is above a certain threshold because of the porous electrode structure and the charge redistribution process [43], the delivered charge will not increase anymore if a sufficiently small discharge current is applied to exhaust the total available charge given the finite voltage and capacitance of the supercapacitor. Therefore, there exists a minimum discharge current below which the delivered charge discontinues to increase. When the discharge current is sufficiently small, the discharge time is extended and the self-discharge process results in a significant energy loss, which ultimately leads to a drop in the delivered charge, as elaborated in Section II-B using simulation results.

Second, the delivered charge pattern shows some fine structures when the discharge current is below the threshold. In some cases, the delivered charge monotonically decreases when the discharge current decreases: Figs. 2(a), 2(d), and 3. On the other hand, the delivered charge remains approximately constant when the discharge current is within a certain range: Figs. 2(b) (0.01–0.005 A), 2(c) (0.005–0.0025 A), 4(a) (0.07–0.014 A), and 4(b) (0.014–0.007 A). This is because of the limited accuracy and precision of the delivered charge data as well as the relatively sparse discharge current values swept. Therefore, it can be anticipated that there exists a certain discharge current at which the delivered charge peaks if the discharge current is more densely swept with a smaller step, as elaborated in Section II-B using simulation results.

Third, the discharge current threshold varies with the initial voltage and the supercapacitor sample. The threshold for sample 2 is 0.01 A at 2.7 and 2 V and 0.005 A at 1.35 and 0.7 V. For sample 1, it is 0.01 A at 2.7 and 2 V and 0.005 A at 1.35 and 0.7 V. The threshold is 0.07 A at 2.7 V and 0.014 A at 2, 1.35, and 0.7 V for sample 3. Since the three samples are made by different manufacturers and their specifications vary in terms of parameters such as rated capacitance and leakage current, the similarities in their delivered charge patterns suggest that the relationship between the delivered charge and the discharge current can be utilized by a variety of supercapacitors with different ratings. As for the discharge current threshold above which Peukert's law applies, a rigorous and systematic study needs to be conducted to examine the effects of various factors such as supercapacitor manufacturer, device chemistry, rated capacitance, rated voltage, leakage current, temperature, and aging condition on this parameter, which is beyond the scope of this paper and will be addressed in the succeeding work.

B. Effects of Porous Electrode Structure, Charge Redistribution, and Self-discharge

To investigate the physical mechanisms leading to the relationship between the delivered charge and the discharge current observed in Section II-A, a generic RC ladder circuit model for 100 F supercapacitors is conceived and analyzed, as shown in Fig. 5. Compared to the model used in [43], this model keeps the five RC branches (R_1 through C_5) to capture the distributed nature of the supercapacitor capacitance and resistance, which is a result of the porous electrode structure and also the origin of the charge redistribution process. This model also incorporates a parallel leakage resistor R_6 to represent the self-discharge process. The supercapacitor terminal voltage is denoted as V_T , which is a measurable parameter. In fact, V_T equals the voltage across the first RC branch composed of R_1 and C_1 . During a charging or discharging process, the source or load is applied to the supercapacitor terminals and the capacitor of each RC branch is accessed through a series connection of all resistors from the supercapacitor terminals to the branch in question. The time constant of each RC branch can be written as

$$\tau_i = C_i \sum_{k=1}^i R_k, \quad (2)$$

and the porous electrode theory gives that

$$\tau_1 < \tau_2 < \dots < \tau_n. \quad (3)$$

The component values of the five RC branches are tuned to generate time constants that can be used to characterize the supercapacitor behavior on various time scales: $\tau_1 = 1.05$, $\tau_2 = 10$, $\tau_3 = 100$, $\tau_4 = 1000$, and $\tau_5 = 10000$ s. The total capacitance of the five branch capacitors is 100 F. The first branch capacitance is 70% of the total capacitance because this is the major branch. The capacitances are 16, 8, 4, and 2 F for the remaining four branches with a scale factor of 0.5 based on the fact that a slower branch makes a smaller contribution to the total capacitance. As for resistors, the first branch resistance is based on the typical

ESR value specified in the sample 2 datasheet. The other four resistances are calculated based on the time constants and capacitances using (2). As for the parallel leakage resistor R_6 , its value is estimated based on the rated voltage and the leakage current specified in the sample 2 datasheet. It should be noted that this model is conceived to explain the impact of supercapacitor physics on the delivered charge. The model component values are assumed with certain arbitrariness and they are not determined by characterizing the supercapacitor sample because it is experimentally challenging to identify the component values in an effective manner. In fact, the self-discharge process is simplified to a great extent and only a constant leakage resistor R_6 is used to represent this complex process [9]–[13].

To illustrate the effects of supercapacitor physics on the delivered charge pattern shown in Fig. 2(a), the model shown in Fig. 5 is simulated using LTspice. The simulation setup and results are as follows. The initial voltages of the five branch capacitors are set to be 2.7 V and the discharge current is swept. For each current, the delivered charge associated with the cutoff voltage of 0.01 V is calculated and plotted, as shown in Fig. 6. To demonstrate the effects of self-discharge, this plot includes two sets of data obtained from two configurations of the model: one with R_6 and the other without R_6 . It can be observed that these two datasets overlap when the discharge current decreases from 50 to 0.05 A and separate for 0.05–0.001 A. The model with R_6 results in a delivered charge pattern consistent with the experiment results shown in Fig. 2(a). Specifically, Peukert's law applies for the current range of 0.01–50 A and does not apply for 0.001–0.01 A. On the other hand, although the model without R_6 leads to a delivered charge pattern consistent with the experiment results for 0.01–50 A, it does not correctly predict the pattern for 0.001–0.01 A because the self-discharge process is not taken into account.

As shown in Figs. 2(a) and 6, different patterns are observed for the delivered charge when the discharge current varies, which are due to the combined effects of the porous electrode structure and the charge redistribution and self-discharge processes. Previous studies [34]–[37] have revealed that the impact of charge redistribution on supercapacitor voltage change and energy loss is more significant during a relatively short term while self-discharge needs to be taken into account in the long term. When the discharge current is relatively large (i.e., 10–0.01 A in Fig. 2(a) or 50–0.05 A in Fig. 6), the discharge time is relatively short. Therefore, the charge redistribution process dominates and the impact of self-discharge is negligible. As analyzed in [43], due to the distributed nature of the supercapacitor capacitance and resistance and the charge redistribution process, more charge is extracted if the discharge current is smaller and therefore Peukert's law applies. If the discharge current is sufficiently small (i.e., 0.01–0.0025 A in Fig. 2(a) or 0.05–0.001 A in Fig. 6), the discharge time is extended and the significant impact of self-discharge on energy loss needs to be taken into account, which results in a drop in the delivered charge.

To illustrate the fine structures of the delivered charge pattern, the discharge current in Fig. 6 is densely swept between the range of 0.05–0.005 A. The delivered charge peaks at 263.232 C at 0.01 A if rounded to thousandths. The two neighboring points are 263.067 C at 0.02 A and 263.110 C at 0.009 A. With this configuration of significant figures, the delivered charge decreases monotonically when the discharge current decreases from 0.01 to 0.001 A. On the

other hand, if all three delivered charge values are rounded to 263 C, the pattern of the delivered charge flattens between the range of 0.009–0.02 A.

The effects of the supercapacitor porous electrode structure and the charge redistribution and self-discharge processes on the delivered charge are analyzed for two discharge currents: 1 and 0.005 A. The simulation results for the 1 A current are shown in Fig. 7. Specifically, Fig. 7(a) plots the simulated supercapacitor terminal and five branch capacitor voltages using the model shown in Fig. 5 when R_6 is present. As analyzed in [43], when a discharge current is applied to bring the supercapacitor terminal voltage down to the cutoff voltage, the charge stored in the RC branches is extracted progressively from the first branch with the smallest time constant to the last branch with the largest time constant. A smaller discharge current requires a longer time to reduce the supercapacitor terminal voltage (mainly the voltage across the first branch capacitor) to the cutoff voltage. As the discharge time extends, more charge stored in slow branches with large time constants is extracted. In the meantime, the charge stored in slow branches redistributes to fast branches, which decelerates the drop in the terminal voltage and prolongs the discharge time.

As shown in Fig. 7(a), the terminal voltage V_T almost overlaps with V_1 . Charge is mainly extracted from C_1 and its voltage drops rapidly. Because of the increasingly larger time constant of the corresponding branch, the drop in $V_2 - V_5$ becomes smaller at a particular point of time compared to the drop in V_1 . Given the voltage differences between $V_2 - V_5$ and V_1 , charge is unidirectionally redistributed from $C_2 - C_5$ to C_1 during the entire discharging process, which decelerates the drop in V_1 . When the discharge current is smaller, these effects are more significant and therefore more charge is extracted from the supercapacitor. Consequently, the final values of the branch capacitor voltages at the end of the discharging process are lower, i.e., the supercapacitor is closer to be fully discharged. As shown in Fig. 7(a), the final voltages at $t=240.553$ s are $V_T=0.010$, $V_1=0.025$, $V_2=0.179$, $V_3=1.150$, $V_4=2.560$, and $V_5=2.667$ V for 1 A. For comparisons, Fig. 8(a) shows the results for 0.005 A and the final voltages at $t=52321.137$ s are $V_T=V_1=0.010$, $V_2=0.011$, $V_3=0.019$, $V_4=0.076$, and $V_5=0.270$ V. Clearly, more charge is extracted when the discharge current is 0.005 A because the branch capacitors are more deeply discharged.

While it is obvious that the delivered charge increases when the discharge current decreases if the discharge current is above a certain threshold, the increase rate of the delivered charge becomes lower when the discharge current is smaller. The increase rate can be quantified in terms of the increase in the delivered charge when the discharge current decreases by a factor of ten (i.e., one decade). Take the 2.7 V experiment of sample 2 for instance. As shown in Fig. 2(a), the delivered charge increases when the discharge current decreases from 10 to 0.01 A. The increase in the delivered charge is 21.46 C when the discharge current decreases from 10 to 1 A. The increase rate can be denoted as 21.46 C/dec for the current range of 10–1 A. For 1–0.1 and 0.1–0.01 A, the rate is 15.08 and 12.33 C/dec, respectively. A similar pattern is observed in Fig. 6. For the three current ranges of 10–1, 1–0.1, and 0.1–0.01 A, the rate is 38.44, 17.20, and 5.47 C/dec, respectively. The decaying increase rate of the delivered charge is due to the smaller capacitance and therefore the less charge contributed by a slower branch with a larger time constant when a smaller discharge current is applied, which can be intuitively explained using the model shown in Fig. 5. Suppose a

discharge current I_0 fully discharges C_1 through C_3 and leaves C_4 and C_5 still fully charged (i.e., 2.7 V) at the end of the discharging process. Then a smaller discharge current (e.g., $0.1I_0$) fully discharges C_4 and leaves C_5 still intact. In this case, the delivered charge is increased by 10.8 C ($Q = C_4 V = 4 \times 2.7 = 10.8$ C, the cutoff voltage is assumed to be 0 V). Finally, an even smaller discharge current (e.g., $0.01I_0$) fully discharges C_5 and the delivered charge is increased by 5.4 C compared to that resulted from $0.1I_0$.

The impact of self-discharge on the delivered charge can be illustrated using Figs. 7(b) and 8(b). During the entire discharging phase, energy is dissipated by R_6 representing the self-discharge process. For 1 A, since the discharge time is relatively short (i.e., 240.553 s), the effect of self-discharge is insignificant. In fact, Fig. 7(b) compares two sets of V_T and V_5 : one with R_6 and the other without R_6 . It can be observed that when R_6 is present, V_5 is slightly lower at the end of the discharging phase: 2.667 V compared to 2.699 V when R_6 is not present. On the other hand, the impact of self-discharge becomes significant during the extended discharging phase if the discharge current is sufficiently small. As shown in Fig. 8(b), when R_6 is present, V_5 drops much faster compared to the case in which R_6 is not present. At the end of the discharging phase, V_5 is 0.270 V when R_6 is present and 0.563 V when R_6 is not present, respectively. Consequently, V_T reaches the cutoff voltage faster (52321.137 versus 53495.159 s) and the delivered charge is less (261.606 versus 267.476 C) when self-discharge is taken into account. In summary, when a smaller discharge current is applied, the porous electrode structure and the charge redistribution process result in an increase in the delivered charge while self-discharge leads to a drop.

III. Lower Bound of Utilized Charge Capacity

A. Experiments and Results

As investigated in [43], the lower bound of the utilized charge capacity is achieved when the supercapacitor is only partially charged to the desired initial voltage using the largest possible current specified in the supercapacitor datasheet. Take sample 2 for instance. Fig. 9 shows a 10 A experiment when the initial voltage of the constant current discharge process is 2.7 V. Similar to the experiment shown in Fig. 1 for studying the upper bound of the utilized charge capacity, this experiment also includes three phases. The first phase is composed of ten charging-redistribution-discharging cycles to minimize the effect of residual charge. The third phase uses ten discharging-redistribution cycles to estimate the total charge capacity and the first of these ten cycles is used to determine the utilized charge capacity. While the first and third phases of the lower bound experiment use the same settings as those in the upper bound experiment, the second phase is modified. The supercapacitor is discharged by a constant voltage source of 0.01 V for 3 hours to approximate the ideal condition that the supercapacitor is completely discharged before the charging phase is initiated. It is then charged by a constant current source of 10 A to 2.7 V. After that, a 10 A discharge current is applied and the third phase of the experiment begins. Taking 2.7 V as the initial voltage and 0.01 V as the cutoff voltage, the delivered charge is 231.1 C for the experiment shown in Fig. 9. On the other hand, the total charge capacity estimated using the ten discharging-redistribution cycles and the charging phase is 242.9 and 250.8 C, respectively.

The lower bound of the utilized charge capacity is also investigated using the three supercapacitor samples at various initial voltages. Fig. 10 shows the results for sample 2. Part of the results for samples 1 and 3 are shown in Figs. 11 and 12. Similar patterns of the delivered charge are observed for the three samples at different voltages. Specifically, there exists a discharge current that results in the peaking delivered charge. When the discharge current is larger than this threshold, the delivered charge increases when the discharge current decreases. If the discharge current is below this threshold, fine structures exist: the delivered charge either monotonically decreases when the discharge current decreases or remains approximately constant when the discharge current is within a certain range. The discharge current threshold is dependent on the initial voltage and the supercapacitor sample.

It should be noted that although the delivered charge increases when the discharge current is above the threshold in the lower bound case, which is similar to the pattern observed in the upper bound case, the increase rate is lower. Consider the upper and lower bounds of sample 2 at 2.7 V. For the upper bound shown in Fig. 2(a), the increase rate is 21.46, 15.08, and 12.33 C/dec for 10–1, 1–0.1, and 0.1–0.01 A, respectively. As shown in Fig. 10(a), the increase rate in the lower bound case is 10.79, 1.43, and 1.09 C/dec, respectively. For each of the three current ranges, the increase rate in the lower bound case is lower compared to that in the upper bound case. This is because the slow branch capacitors of the supercapacitor are fully charged in the upper bound case and only partially charged in the lower bound case. Therefore, when the same branch capacitor is fully discharged, a smaller amount of charge is extracted in the lower bound case.

B. Effects of Porous Electrode Structure, Charge Redistribution, and Self-discharge

The delivered charge pattern observed in Section III-A can also be explained using the model shown in Fig. 5. The simulation setup and results for 2.7 V are as follows. The initial voltages of the five branch capacitors are set to be 0 V. A constant current source of 10 A is applied and the supercapacitor terminal voltage reaches 2.7 V at 20.3 s. The charging current is then removed and the discharging current is connected. Fig. 13 shows the simulated patterns with and without R_6 . Clearly, the pattern with R_6 is consistent with the experiment results and the one without R_6 is not when the discharge current is sufficiently small. When R_6 is present, the delivered charge peaks at 199.40 C at 0.01 A. The increase rate of the delivered charge is 19.10, 5.50, and 1.81 C/dec for 10–1, 1–0.1, and 0.1–0.01 A, respectively. Therefore, the increase rate in the lower bound case is significantly lower compared to the corresponding rate in the upper bound case, as shown in Fig. 6, which is also consistent with the experiment results.

The effects of the porous electrode structure and the charge redistribution and self-discharge processes are illustrated using the 1 and 0.005 A simulation results shown in Figs. 14 and 15. As shown in Fig. 14(a), the charging process using a large current mainly charges the first branch capacitor and the slow branch capacitors are not fully charged. In fact, the five branch capacitor voltages $V_1 - V_5$ are 2.550, 1.471, 0.116, 0.001 and 0.000 V at the end of the charging process ($t=20.3$ s). When the discharge current is applied, charge is first extracted from C_1 . Although V_1 drops continuously, it is still greater than $V_2 - V_5$ during

certain periods of time and therefore charge is transferred from C_1 to $C_2 - C_3$. Take V_3 for instance. It increases from 0.116 V ($t=20.3$ s) to 1.067 V ($t=120.102$ s) after the charging current is removed because during this period of time charge is redistributed from C_1 and C_2 to C_3 . As the discharging process continues, C_3 is accessed by the discharge current and its voltage drops. As long as V_3 is greater than V_1 and V_2 , a portion of charge flows back from C_3 to C_1 and C_2 . Therefore, different from the upper bound case shown in Fig. 7, charge redistribution in the lower bound case is bidirectional during the entire discharging process: charge redistributes from fast branches to slow branches during the early stage and the charge transfer direction is reversed during the late stage. When the entire discharging process is considered, the charge stored in slow branches will be partially or completely extracted depending on the discharge current. Compare the final values of the five branch capacitor voltages shown in Figs. 14(a) and 15(a): 0.025, 0.161, 0.744, 0.157, and 0.001 V for 1 A and 0.010, 0.011, 0.019, 0.075, and 0.265 V for 0.005 A. Due to the extended discharge time in the 0.005 A case, $C_1 - C_4$ are more deeply discharged and more charge is delivered even with a more significant energy loss due to self-discharge. Therefore, the coupled effects of the porous electrode structure and the charge redistribution process result in an increase in the delivered charge.

The impact of self-discharge is shown in Figs. 14(b) and 15(b). For 1 A, the discharge time is relatively short. Because of charge redistribution, V_5 increases very slowly from the initial value of 0.000 V to the final value of 0.001 V during the discharging phase. Therefore, the energy loss due to R_6 is minimal. In fact, the final value of V_5 is the same as the one when R_6 is not present. When the discharge time is extended, the impact of self-discharge becomes noticeable because charge redistribution results in a significantly large V_5 , as shown in Fig. 15(b). If the discharge current is even smaller (e.g., 0.001 A), the energy loss due to self-discharge is even more significant and the delivered charge drops, as shown in Fig. 13.

IV. Comparisons of Utilized Charge Capacity Bounds

This section compares the upper and lower bounds of the utilized charge capacity by quantifying the difference between them as follows:

$$\delta_U = \frac{U_{max} - U_{min}}{Q_{rated}} \times 100\%, \quad (4)$$

where U_{max} is the upper bound, U_{min} is the lower bound, and Q_{rated} is the rated charge capacity determined using the rated voltage and the rated capacitance. The difference between the upper and lower bounds is normalized with respect to the rated charge capacity to compare the results for the three supercapacitor samples with different rated capacitances. The results are shown in Fig. 16.

The following observations can be made. First, the difference between the upper and lower bounds of the utilized charge capacity is significant for all samples at all voltages and discharge currents. The maximum difference is observed for sample 1 at 0.01 A when the

initial voltage is 2.7 V: 23.5% or 6.35 C. The minimum is observed for sample 1 at 1 A when the initial voltage is 0.7 V: 1.89% or 0.51 C. Second, the difference is dependent on the supercapacitor sample. In general, the differences for samples 1 and 2 are at the same level, which are greater than those for sample 3. Considering the fact that the three samples vary in terms of manufacturer, rated capacitance, leakage current, and other specifications, further work needs to be conducted to examine the mechanisms leading to these differences. Third, for a specific sample, the difference is greater at a higher initial voltage. This is because of the voltage dependency of capacitance: a higher voltage results in a larger capacitance. Therefore, more charge is stored in slow branch capacitors at a higher voltage. Finally, the difference is also dependent on the discharge current. The pattern of the difference is similar to those of the delivered charge (both the upper and lower bounds): the difference peaks at a certain discharge current.

V. Comparisons of Total Charge Capacity Bounds

In addition to the utilized charge capacity delivered during a discharging process, the total available charge stored in the supercapacitor is also a crucial parameter. To estimate the total charge capacity, the experiments during which the impact of self-discharge is significant are excluded and only those with discharge currents above the threshold are included. The reason is that the total charge capacity estimated using the experiment with a discharge current below the threshold underestimates the actual value. For instance, to estimate the total charge capacity for sample 2, only seven experiments (i.e., 10, 5, 1, 0.5, 0.1, 0.05, and 0.01 A) are used and the 0.005 and 0.0025 A experiments are excluded. The average of the seven total charge capacity values is used as the estimate. For the lower bound, in addition to the estimate using the ten discharging-redistribution cycles, another estimate using the constant current charging phase is also determined. The difference between the upper and lower bounds of the total charge capacity is quantified as follows:

$$\delta_Q = \frac{Q_{max} - Q_{min}}{Q_{rated}} \times 100\%, \quad (5)$$

$$\delta_Q^* = \frac{Q_{max} - Q_{min}^*}{Q_{rated}} \times 100\%, \quad (6)$$

where Q_{max} is the upper bound, Q_{min} is the lower bound estimated using the discharging-redistribution cycles, Q_{min}^* is the lower bound estimated using the charging phase, and Q_{rated} is the rated charge capacity determined using the rated voltage and the rated capacitance. The results are shown in Fig. 17.

Referring to those observations made on the utilized charge capacity, some also apply to the total charge capacity. Consistent with [43], the Q_{min}^* estimate is greater than the Q_{min} estimate. Therefore, δ_Q^* is less than δ_Q . The difference is significant for all samples at all

voltages even in terms of δ_Q^* . The difference varies with the sample. Again, the differences for sample 3 are the smallest. The difference increases when the voltage increases because of the voltage dependency of capacitance.

VI. Conclusion

This paper studies the individual and combined effects of three aspects of the supercapacitor physics on its charge capacity: porous electrode structure, charge redistribution, and self-discharge. The relationship between the delivered charge and the discharge current is examined for both the upper and lower bounds of the utilized charge capacity. By sweeping the initial voltage and the discharge current of the constant current discharge experiment for three supercapacitor samples with different rated capacitances from different manufacturers, a similar pattern of the delivered charge is observed for all samples at all voltages. For both the upper and lower bounds, the delivered charge peaks at a certain discharge current and decreases when the discharge current deviates from this threshold. In the upper bound case, Peukert's law applies when the discharge current is above the threshold and does not apply if the discharge current is below the threshold. In the lower bound case, if the discharge current is above the threshold, the delivered charge increases when the discharge current decreases although the increase rate is lower compared to that in the upper bound case. Moreover, comparisons of the upper and lower bounds of the utilized and total charge capacities show that the difference between the bounds is significant for all samples at all voltages and currents.

The effects of the supercapacitor physics on the utilized charge capacity are illustrated using a five-branch RC ladder circuit model. For both the upper and lower bounds, because of the porous electrode structure, or equivalently, the distributed nature of the capacitance and resistance, slow branch capacitors with large time constants are accessed during the extended discharging phase if a smaller discharge current is applied, which results in an increase in the delivered charge. In the upper bound case, charge redistribution is unidirectional, which is from slow branches to fast branches, during the entire discharging phase because all branch capacitors are fully charged at the beginning. On the other hand, charge redistribution is bidirectional in the lower bound case: from fast branches to slow branches during the early stage and the opposite during the late stage, which is because slow branch capacitors are only partially charged at the beginning. As for self-discharge, its impact is negligible if the discharge current is relatively large. If the discharge current is sufficiently small, the energy loss due to self-discharge during the extended discharging phase is significant, which results in a drop in the delivered charge.

While this paper investigates the effects of supercapacitor physics on its charge capacity at room temperature, it also raises questions about the discharge current threshold, as posed in Section II-A. To reveal the physical mechanisms and factors (e.g., supercapacitor chemistry, manufacturing process, device ratings, aging condition, and temperature) affecting this parameter, extensive theoretical and experimental work needs to be conducted.

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REFERENCES

- [1]. Pandolfo A and Hollenkamp A, "Carbon properties and their role in supercapacitors," *Journal of Power Sources*, vol. 157, no. 1, pp. 11–27, 2006.
- [2]. de Levie R, "On porous electrodes in electrolyte solutions: I. capacitance effects," *Electrochimica Acta*, vol. 8, no. 10, pp. 751–780, 1963.
- [3]. Yaniv M and Soffer A, "The transient behavior of an ideally polarized porous carbon electrode at constant charging current," *Journal of The Electrochemical Society*, vol. 123, no. 4, pp. 506–511, 1976.
- [4]. Lai JS, Levy S, and Rose MF, "High energy density double-layer capacitors for energy storage applications," *IEEE Aerospace and Electronic Systems Magazine*, vol. 7, no. 4, pp. 14–19, 1992.
- [5]. Belhachemi F, Rael S, and Davat B, "A physical based model of power electric double-layer supercapacitors," in *Conference Record of the 2000 IEEE Industry Applications Conference*, 2000, pp. 3069–3076.
- [6]. Nelms RM, Cahela DR, and Tatarchuk BJ, "Modeling double-layer capacitor behavior using ladder circuits," *IEEE Transactions on Aerospace and Electronic Systems*, vol. 39, no. 2, pp. 430–438, 2003.
- [7]. Faranda R, "A new parameters identification procedure for simplified double layer capacitor two-branch model," *Electric Power Systems Research*, vol. 80, no. 4, pp. 363–371, 2010.
- [8]. Buller S, Karden E, Kok D, and Doncker RWD, "Modeling the dynamic behavior of supercapacitors using impedance spectroscopy," *IEEE Transactions on Industry Applications*, vol. 38, no. 6, pp. 1622–1626, 2002.
- [9]. Conway BE, Pell W, and Liu T-C, "Diagnostic analyses for mechanisms of self-discharge of electrochemical capacitors and batteries," *Journal of Power Sources*, vol. 65, no. 1, pp. 53–59, 1997.
- [10]. Ricketts B and Ton-That C, "Self-discharge of carbon-based supercapacitors with organic electrolytes," *Journal of Power Sources*, vol. 89, no. 1, pp. 64–69, 2000.
- [11]. Diab Y, Venet P, Gualous H, and Rojat G, "Self-discharge characterization and modeling of electrochemical capacitor used for power electronics applications," *IEEE Transactions on Power Electronics*, vol. 24, pp. 510–517, 2009.
- [12]. Zhang Y and Yang H, "Modeling and characterization of supercapacitors for wireless sensor network applications," *Journal of Power Sources*, vol. 196, no. 8, pp. 4128–4135, 2011.
- [13]. Yang H and Zhang Y, "Self-discharge analysis and characterization of supercapacitors for environmentally powered wireless sensor network applications," *Journal of Power Sources*, vol. 196, no. 20, pp. 8866–8873, 2011.
- [14]. Zubieta L and Bonert R, "Characterization of double-layer capacitors for power electronics applications," *IEEE Transactions on Industry Applications*, vol. 36, no. 1, pp. 199–205, 2000.
- [15]. Graydon JW, Panjehshahi M, and Kirk DW, "Charge redistribution and ionic mobility in the micropores of supercapacitors," *Journal of Power Sources*, vol. 245, pp. 822–829, 2014.
- [16]. Sedlakova V, Sikula J, Majzner J, Sedlak P, Kupařowitz T, Buegler B, and Vasina P, "Supercapacitor equivalent electrical circuit model based on charges redistribution by diffusion," *Journal of Power Sources*, vol. 286, pp. 58–65, 2015.
- [17]. Szweczyk A, Sikula J, Sedlakova V, Majzner J, Sedlak P, and Kupařowitz T, "Voltage dependence of supercapacitor capacitance," *Metrology and Measurement Systems*, vol. 23, no. 3, pp. 403–411, 2016.

- [18]. Schonberger J and GmbH P Modeling a supercapacitor using PLECS. [Online]. Available: https://plexim.com/files/plecs_supercap.pdf
- [19]. Spyker R and Nelms R, "Analysis of double-layer capacitors supplying constant power loads," IEEE Transactions on Aerospace and Electronic Systems, vol. 36, no. 4, pp. 1439–1443, 2000.
- [20]. Mellincovsky M, Kuperman A, Lerman C, Gadelovits S, Aharon I, Reichbach N, Geula G, and Nakash R, "Performance and limitations of a constant power-fed supercapacitor," IEEE Transactions on Energy Conversion, vol. 29, no. 2, pp. 445–452, 2014.
- [21]. Yang H and Zhang Y, "Estimation of supercapacitor energy using a linear capacitance for applications in wireless sensor networks," Journal of Power Sources, vol. 275, pp. 498–505, 2015.
- [22]. Yang H and Zhang Y, "Characterization of supercapacitor models for analyzing supercapacitors connected to constant power elements," Journal of Power Sources, vol. 312, pp. 165–171, 2016.
- [23]. Rafik F, Gualous H, Gallay R, Crausaz A, and Berthon A, "Frequency, thermal and voltage supercapacitor characterization and modeling," Journal of Power Sources, vol. 165, no. 2, pp. 928–934, 2007.
- [24]. Reichbach N, Mellincovsky M, Peretz MM, and Kuperman A, "Long-term wide-temperature supercapacitor ragone plot based on manufacturer datasheet," IEEE Transactions on Energy Conversion, vol. 31, no. 1, pp. 404–406, 2016.
- [25]. Ktz R, Ruch P, and Cericola D, "Aging and failure mode of electrochemical double layer capacitors during accelerated constant load tests," Journal of Power Sources, vol. 195, no. 3, pp. 923–928, 2010.
- [26]. Marracci M, Tellini B, Catelani M, and Ciani L, "Ultracapacitor degradation state diagnosis via electrochemical impedance spectroscopy," IEEE Transactions on Instrumentation and Measurement, vol. 64, no. 7, pp. 1916–1921, 2015.
- [27]. Moayedi S, Cingoz F, and Davoudi A, "Accelerated simulation of high-fidelity models of supercapacitors using waveform relaxation techniques," IEEE Transactions on Power Electronics, vol. 28, no. 11, pp. 4903–4909, 2013.
- [28]. Nadeau A, Hassanaliagh M, Sharma G, and Soyata T, "Energy awareness for supercapacitors using Kalman filter state-of-charge tracking," Journal of Power Sources, vol. 296, pp. 383–391, 2015.
- [29]. Zhang L, Wang Z, Sun F, and Dorrell DG, "Online parameter identification of ultracapacitor models using the extended kalman filter," Energies, vol. 7, no. 5, pp. 3204–3217, 2014.
- [30]. Reichbach N and Kuperman A, "Recursive-least-squares-based real-time estimation of supercapacitor parameters," IEEE Transactions on Energy Conversion, vol. 31, no. 2, pp. 810–812, 2016.
- [31]. Eddahech A, Ayadi M, Briat O, and Vinassa J-M, "Online parameter identification for real-time supercapacitor performance estimation in automotive applications," International Journal of Electrical Power & Energy Systems, vol. 51, pp. 162–167, 2013.
- [32]. Chaoui H and Gualous H, "Online lifetime estimation of supercapacitors," IEEE Transactions on Power Electronics, vol. 32, no. 9, pp. 7199–7206, 2017.
- [33]. Black J and Andreas HA, "Effects of charge redistribution on self-discharge of electrochemical capacitors," Electrochimica Acta, vol. 54, no. 13, pp. 3568–3574, 2009.
- [34]. Yang H and Zhang Y, "Analysis of supercapacitor energy loss for power management in environmentally powered wireless sensor nodes," IEEE Transactions on Power Electronics, vol. 28, no. 11, pp. 5391–5403, 2013.
- [35]. Yang H and Zhang Y, "A study of supercapacitor charge redistribution for applications in environmentally powered wireless sensor nodes," Journal of Power Sources, vol. 273, pp. 223–236, 2015.
- [36]. Yang H, "Analysis of supercapacitor charge redistribution through constant power experiments," in Proceedings of the 2017 IEEE Power & Energy Society General Meeting (PESGM 2017), 2017, p. in press.
- [37]. Yang H, "Bounds of supercapacitor open-circuit voltage change after constant power experiments," in Proceedings of the 10th Electrical Energy Storage Applications and Technologies (EESAT 2017), 2017, p. in press.

- [38]. Yang H, "Impact of charge redistribution on delivered energy of supercapacitors with constant power loads," in Proceedings of the 2018 IEEE Applied Power Electronics Conference and Exposition (APEC 2018), 2018, p. in press.
- [39]. Chai R and Zhang Y, "A practical supercapacitor model for power management in wireless sensor nodes," IEEE Transactions on Power Electronics, vol. 30, no. 12, pp. 6720–6730, 2015.
- [40]. Yang H and Zhang Y, "A task scheduling algorithm based on supercapacitor charge redistribution and energy harvesting for wireless sensor nodes," Journal of Energy Storage, vol. 6, pp. 186–194, 2016.
- [41]. Yang H and Zhang Y, "Power management in supercapacitor-based wireless sensor nodes," in Supercapacitor Design and Applications, 2016, pp. 165–179.
- [42]. Ju Q and Zhang Y, "Charge redistribution-aware power management for supercapacitor-operated wireless sensor networks," IEEE Sensors Journal, vol. 16, no. 7, pp. 2046–2054, 2016.
- [43]. Yang H, "Estimation of supercapacitor charge capacity bounds considering charge redistribution," IEEE Transactions on Power Electronics, p. in press, 2017.
- [44]. Torregrossa D, Bahramipناه M, Namor E, Cherkaoui R, and Paolone M, "Improvement of dynamic modeling of supercapacitor by residual charge effect estimation," IEEE Transactions on Industrial Electronics, vol. 61, no. 3, pp. 1345–1354, 2014.
- [45]. Doerffel D and Sharkh SA, "A critical review of using the peukert equation for determining the remaining capacity of lead-acid and lithium-ion batteries," Journal of Power Sources, vol. 155, no. 2, pp. 395–400, 2006.

Fig. 1.
Upper bound case: a 10 A constant current discharge experiment for supercapacitor sample 2.

Fig. 2.

Upper bound case: relationship between delivered charge and discharge current for supercapacitor sample 2. (a) Initial voltage is 2.7 V. (b) Initial voltage is 2 V. (c) Initial voltage is 1.35 V. (d) Initial voltage is 0.7 V.

Fig. 3. Upper bound case: relationship between delivered charge and discharge current for supercapacitor sample 1. (a) Initial voltage is 2.7 V. (b) Initial voltage is 0.7 V.

Fig. 4.

Upper bound case: relationship between delivered charge and discharge current for supercapacitor sample 3. (a) Initial voltage is 2.7 V. (b) Initial voltage is 0.7 V.

Fig. 5.
A five-branch RC ladder circuit model for 100 F supercapacitors.

Fig. 6. Upper bound case: simulated relationship between delivered charge and discharge current for 100 F supercapacitors.

Fig. 7. Upper bound case: simulation results for 1 A current. (a) Supercapacitor terminal and branch capacitor voltages. (b) Effects of R_6 on V_T and V_5 .

Fig. 8. Upper bound case: simulation results for 0.005 A current. (a) Supercapacitor terminal and branch capacitor voltages. (b) Effects of R_6 on V_T and V_5 .

Fig. 9.
Lower bound case: a 10 A constant current discharge experiment for supercapacitor sample 2.

Fig. 10.

Lower bound case: relationship between delivered charge and discharge current for supercapacitor sample 2. (a) Initial voltage is 2.7 V. (b) Initial voltage is 2 V. (c) Initial voltage is 1.35 V. (d) Initial voltage is 0.7 V.

Fig. 11.
Lower bound case: relationship between delivered charge and discharge current for supercapacitor sample 1. (a) Initial voltage is 2.7 V. (b) Initial voltage is 0.7 V.

(a)

(b)

Fig. 12.

Lower bound case: relationship between delivered charge and discharge current for supercapacitor sample 3. (a) Initial voltage is 2.7 V. (b) Initial voltage is 0.7 V.

Fig. 13. Lower bound case: simulated relationship between delivered charge and discharge current for 100 F supercapacitors.

Fig. 14.

Lower bound case: simulation results for 1 A current. (a) Supercapacitor terminal and branch capacitor voltages. (b) Effects of R_6 on V_T and V_5 .

Fig. 15. Lower bound case: simulation results for 0.005 A current. (a) Supercapacitor terminal and branch capacitor voltages. (b) Effects of R_6 on V_T and V_5 .

Fig. 16. Normalized difference between upper and lower bounds of utilized charge capacity. (a) Sample 1. (b) Sample 2. (c) Sample 3.

Fig. 17.
Normalized difference between upper and lower bounds of total charge capacity.

TABLE I

Supercapacitor Samples.

Sample	1	2	3
Manufacturer	Eaton	AVX	Maxwell
Model	HV1030-2R7106-R	SCCV60B107MRB	BCAP0350
Capacitance (F)	10	100	350
Voltage (V)	2.7	2.7	2.7