Investigation on Capacitance Regeneration Characteristics of Supercapacitors during the Aging Tests

L. Zhang¹, H L Shi¹, L Q Wang¹ and N Wang¹

1 School of Electrical Engineering, Dalian University of Technology, China
E-mail: zhanglii@dlut.edu.cn

Abstract: The lifetime prediction of supercapacitors is of great significance to the management of energy storage systems, but the phenomenon of capacitance regeneration may occur in the aging cycle experiment of supercapacitors, which will bring about interference to its lifetime prediction. In this paper, the critical factors affecting the capacitance regeneration of supercapacitors are investigated, so as to analyze the influence of the regeneration phenomenon on the lifetime prediction of supercapacitors. The results show that the regeneration performance of supercapacitors is closely related to the working voltage, temperature, aging depth and recovery time. When the charging voltage is increased, the amplitude of the capacitance regeneration decreases, and with the deepening of aging degree, the amplitude of the capacitance regeneration decreases gradually. The temperature has little effect on the amplitude of the capacitance regeneration, but the higher the temperature, the longer the recovery time of capacitance regeneration. In addition, the regeneration capacitance of supercapacitors decays faster than its inherent capacitance under the same aging test conditions. Considering the capacitance regeneration characteristics, the aging trend of supercapacitors is predicted by using support vectors machines method. The prediction results are basically identical with the experimental results.

1. Introduction
Supercapacitors have a wide application prospect in energy storage field. Due to the low work voltage of the supercapacitor cell, the series-parallel combinations of many supercapacitors are usually needed in the energy storage system. If a supercapacitor cell is broken, then the entire energy storage system will fail. Therefore, the lifetime prediction of the supercapacitors is of great significance [1-2]. To ensure the performances and functionalities of the energy storage system during its lifetime, the reliability of supercapacitors should be quantified by accelerated ageing tests [3]. Thus the power cycling charge-discharge test has been presented [4]. The work mode of supercapacitors usually includes the charge-discharge state and the static recovery state. For the charge and discharge performance of supercapacitors, a lot of experimental studies have been done, but little research has been done on the static recovery characteristics of supercapacitors. The static recovery of supercapacitors after the charge-discharge cycling tests can leads to an increase in capacitance [5], it is so called the capacitance regeneration phenomenon of supercapacitors. The capacitance regeneration can maintain the energy storage capacity of the supercapacitors to a certain degree and prolong its lifetime, but it can also bring about interference to the lifetime prediction of supercapacitors [6-8]. Therefore the researches of static recovery performance after charge-discharge cycling tests are also necessary. In this paper, the capacitance regeneration phenomenon of supercapacitors are investigated during the aging tests, the effects of charging voltage, temperature, aging depth and the recovery time on the capacitance regeneration are discussed, the database of these experiments is further used to study the lifetime prediction of supercapacitors.
2. Capacitance degeneration during the aging tests

The experimental samples are the same batch of supercapacitors with a rated voltage of 2.7V, a nominal capacitance of 10F, and an ambient temperature range of -40°C to +65°C. In order to achieve the aim of accelerating aging, a constant current charge-discharge cycling test system of the supercapacitors is established. The schematic diagram is shown in figure 1. The charge-discharge current is 3A, other experimental conditions of the aging tests are listed in table 1.

![Principle diagram of aging experiment for supercapacitors](image)

**Figure 1.** Principle diagram of aging experiment for supercapacitors.

| Sample number | Charging Voltage (V) | Temperature (°C) |
|---------------|----------------------|------------------|
| 1# (1*)       | 2.7                  | 25               |
| 2#            | 3.2                  | 25               |
| 3#            | 2.7                  | 50               |
| 4#            | 2.7                  | 65               |
| 5# (5*)       | 3.2                  | 65               |

First, the constant current charge-discharge cycling tests are carried out on 1# supercapacitor sample. The charge-discharge current is 3A, the charging voltage is 2.7V, the experimental temperature is 25°C. As shown in figure 2, the capacitance value of the supercapacitor gradually decreases with the increase of the aging cycle times. When 4000 times cycling, the power cycling test was stopped, at this time the capacitance of the supercapacitor has dropped to 10.825F. Next the supercapacitor was in a state of static recovery, the capacitance regeneration phenomenon could be observed by measuring the capacitance value of the supercapacitor. Clearly the capacitance value gradually increased, after 13 hours the capacitance value stabilized at 11.0375F. It shows that during the power cycling test, the interval can cause the capacitance of the supercapacitor to increase, if the percentage of the capacitance increment to its initial capacitance value is called the amplitude of the capacitance regeneration, the amplitude of the capacitance regeneration of the 1# supercapacitor is 1.96%.

Then continuing the aging cycling tests, it is easy to see the capacitance of the supercapacitor still decreases with the increase of the aging cycling times. When the capacitance drops from 11.0375F to 10.825F once more, it has gone through 900 times cycling, $n_2 = 900$. However, at the beginning of the aging tests the capacitance reduced from 11.0375F to 10.825F, which had experienced 3200 times cycling, $n_1 = 3200$. Obviously, $n_1 > n_2$, this explains that the regeneration capacitance of the supercapacitor decays faster than its inherent capacitance under the same aging test conditions.

As shown in figure 3, the aging trend of the 1# and 1* supercapacitor samples are compared. The experimental conditions of the two supercapacitors are the same. Among them, the 1* supercapacitor was always in the state of continuous cyclic charging-discharging tests, there was no the capacitance regeneration phenomenon during the aging tests. In contrast, cyclic charging-discharging tests of the 1# supercapacitor were selected to interrupt at different aging stages, the duration of every interruption was about several hours. During this period, the capacitance value was measured until the capacitance value was stable. It can be seen that the capacitance regeneration phenomenon of the 1# supercapacitor occurs during every interruption.
Figure 2. Regeneration phenomenon of supercapacitor.

Figure 3. Aging trend of the supercapacitor.

From the beginning of the first regeneration phenomenon, the differentiation of the aging trend of the two supercapacitors appears. Owing to the capacitance regeneration, the capacitance reduction of the 1# supercapacitor is slower than that of the 1* supercapacitor. After 37 thousand times cycling tests, the capacitance of the two supercapacitors decreases by 6.9% and 8.3% respectively. It shows that the regeneration phenomenon of supercapacitors can delay the decline in capacitance, and prolong the lifetime of the supercapacitors.

3. Analysis of capacitance regeneration

3.1. The effect of voltage on characteristics of capacitance regeneration

Constant current cycling charge-discharge tests are done on the 1# and 2# supercapacitor samples. The charge-discharge current is 3A, the charging voltage is rated voltage (2.7V) and 1.2 times rated voltage respectively, the ambient temperature is 25℃. The influence of the maximum charging voltage on characteristics of capacitance regenerative was studied, as shown in figure 4. The interruptions were carried out during aging cycling test, the duration of every interruptions was several hours. It is obvious from figure 4 that the regeneration capacitance of the 1# supercapacitor is greater than that of the 2# supercapacitor. Thus, the increase of charging voltage leads to the decrease of the regenerative capacitance. The main reason is because the electrolyte of supercapacitor is easily decomposed at high voltage. The separated impurities precipitate on the surface of the electrode,

Figure 4. The effect of voltage on capacitance regeneration characteristics.

Figure 5. the effect of ambient temperature on capacitance regeneration characteristics

destroy the porous structure of the electrode surface, and impede the charge embedding and distribution[9]. Therefore, with the increase of the charging voltage, the amplitude of the capacitance regeneration drops. Similarly, the charging voltage increasing can also accelerate the aging of supercapacitors.
3.2. The effect of temperature on characteristics of capacitance regeneration
Two supercapacitor samples, 1# and 3# are tested by the constant current charge-discharge cycling experiments. The charge-discharge current is 3A, the charging voltage is 2.7V, the ambient temperature is 25℃ and 50℃ respectively. During the power cycling tests, the interrupts was also carried out, the duration of every interruptions was still several hours. The influence of the ambient temperature on characteristics of capacitance regenerative was discussed, as shown in figure 5. As can be seen from figure 5, the increase in temperature can significantly accelerate the aging of the supercapacitor[10], but the effect of temperature on the amplitude of capacitance regeneration is not significant, that is, the amplitude of capacitance regeneration of the two supercapacitors is approximately equal. Such as, after 4000 times cycle, the amplitude of the capacitance regeneration of the two supercapacitors is 1.87% and 1.88% respectively, after 27000 times cycle, the amplitude of the capacitance regeneration is 1.23% and 1.25% respectively.

3.3. The effect of aging depth on characteristics of capacitance regeneration
Taking the 1#, 2# and 3# supercapacitors as an example, the characteristics of the capacitance regeneration in different aging depth are shown in figure 6. It is clear from figure 6 that the amplitude of the capacitance regeneration decreases with the increase of aging cycling times. This suggests that the capacitance regeneration ability of supercapacitors decreases gradually as the aging deepens. The stronger the ability of capacitance regeneration, the longer the life of supercapacitors.

3.4. The effect of recovery time on characteristics of capacitance regeneration
After the end of power cycling tests, the capacitance change of the supercapacitor samples is measured with enough time, the relationship between the amplitude of regeneration capacitance and recovery time is observed as shown in figure 7. Figure 7(a) shows the recovery time of the regeneration capacitance of the 1#, 3#, and 4# supercapacitor samples after the end of power cycling tests. Their charging voltage is 2.7V, the experimental temperature is 25℃, 50℃ and 65℃, respectively. It can be noticed that the rising of the regeneration capacitance is fast in the early days, then with the increase of recovery time, the capacitance slowly tend towards stability. The stability time of the regeneration capacitance of the three supercapacitors is 12, 15, and 21 days respectively. This illustrates that the recovery time of the regeneration capacitance increases with the increase in experimental temperature. The reason is that high temperature intensifies the thermodynamic movement of the charge, so it takes a long time for the charge to overcome the thermal stress[11-12]. On the other hand, because of the capacitance regeneration phenomenon, the capacitance of the three supercapacitors increases by 1.058%, 1.0825 and 1.078% respectively. There is little difference between them, this means that the temperature has little effect on the amplitude of the capacitance regeneration.
Figure 7(b) shows the recovery time of the regeneration capacitance of the 4# and 5# supercapacitor samples after the end of power cycling tests. Their experimental temperature both are 65°C, and the charging voltage is 2.7V and 3.2V respectively. It can be seen that the capacitance increases quickly in the beginning, then slowly reaches the stable value, their stability time is 20 and 5 days respectively. The capacitance of the two supercapacitors increases by 1.078% and 1.023% respectively. It shows that the higher the charging voltage, the shorter the recovery time of capacitance regeneration, and the smaller the amplitude of capacitance regeneration. This is mainly due to the fact that the high voltage can lead to electrolyte decomposition, the impurities and by-products blocked the porous structure of the electrode surface [13]. So the path of the charge embedding is shortened, and the recovery time of the charges redistribution is also shortened.

Figure 7. Recovery characterization of regeneration capacitance after ageing test. (a) Recovery time of regeneration capacitance at different temperatures. (b) Recovery time of regeneration capacitance at different voltages.

4. Aging trend prediction

In order to optimize the function of the storage energy system, the database of above experimental results will be used to study the aging trend prediction of supercapacitors. Figure 8 shows the aging trends of the 5# and 5* supercapacitor samples. The experimental conditions of the two supercapacitors are the same, listed in Table 1. As can be seen from figure 8, curve 1 is the aging trend of the 5* supercapacitor which is in the state of continuous cycle charging-discharging test, so there is no the phenomenon of capacitance regeneration. After 55 thousand times cycling, the capacitance attenuation reaches 20%, at this time the supercapacitor is usually considered ineffective. Curve 2 is the aging trend of the 5# supercapacitor, because of the capacitance regeneration phenomenon, the aging trend of the supercapacitor goes down slowly, after 70 thousand times cycling the capacitance drops by 20%. Compared with the 5* supercapacitor, the service life of the 5# supercapacitor is increased by 27%. Curve 3 and 4 from figure 8 is the aging trend prediction of the two supercapacitor samples, the prediction method is a kind of regression fitting based on support vectors machines (SVM), which can effectively deal with the high-dimensional nonlinear fitting of supercapacitors by using fewer samples, finally realize the lifetime prediction.

By using the kernel function of the radial direction, build the SVM model as follows [14]:

$$K(x_i, x) = \exp \left( -\frac{||x_i - x||^2}{2\sigma^2} \right)$$

(1)

where $x_i \in R^N$, it is the N dimension input variable, $\sigma$ is kernel width coefficients. The quality of the SVM model depends on the following parameters, such as penalty parameters $C$, insensitivity coefficients $\varepsilon$, kernel width coefficients $\sigma$ and so on. Therefore, the method of Particle Swarm Optimization (PSO) is used to optimize the parameters of the SVM model. The PSO firstly searches the optimal solution of the particles by using the finite number of iterations, then finds the global optimal solution of the particle swarm. The velocity and position of the particles can be described by formula (2) and (3) [14-15]:

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\[ v_{id}^{k+1} = v_{id}^{k} + c_1 r_1 (p_{id}^{k} - z_{id}^{k}) + c_2 r_2 (p_{id}^{k} - z_{id}^{k}) \]  
\[ z_{id}^{k+1} = z_{id}^{k} + v_{id}^{k+1} \]  

where \( c_1 \) and \( c_2 \) is learning factors, \( r_1 \) and \( r_2 \) is an uniformly distributed random number between 0 and 1, \( k \) is the number of iterations, the particles constantly updates its velocity and position according to formula (2) and (3). \( p_i = (p_{i1}, p_{i2}, ..., p_{id}, ..., p_{id}) \), \( p_i = (p_{i1}, p_{i2}, ..., p_{id}, ..., p_{id}) \), they are respectively the optimum position of the particles and the particle swarm that has been searched at present. The flow of aging trend prediction based on SVM is as follow:

First, SVM model is trained by using experimental data of the aging tests. Next, the PSO is applied to optimize the parameters of SVM model. Finally, the SVM model is retrained by using the optimization parameters, so as to obtain the result of the aging trend prediction, such as curve 3 and curve 4 in figure 8. It can be seen that the aging trend prediction of the supercapacitors is in agreement with the experimental results. Because of taking into account the capacitance regeneration phenomenon, curve 4 is more accord with the actual usage situation of the supercapacitors.

**Figure 8.** Aging trend Prediction.

**Figure 9.** Prediction error analysis of the aging trend.

In different working conditions, the lifetime of supercapacitors is obviously different. In this paper, the aging tests of supercapacitors under different working conditions are carried out. The effect of woking voltage and temperature on the aging trend prediction of supercapacitors is discussed. The aging trend of these supercapacitors are also predicted by SVM method, the prediction errors can be evaluated by the root-mean-square (RMS) error, as shown in figure 9. It can be seen from figure 9 that the prediction error increases as the operating voltage and temperature increase. This is because the supercapacitor may accelerate the aging under the working condition of high temperature and high voltage, resulting in its performance more unstable. When the temperature range is 25°C to 65°C, the working voltage ranges is 2.7V to 3.2V, the RMS error of the aging trend prediction by SVM method is between 0.019 and 0.046, which can meet the requirement of the aging trend prediction of supercapacitors.

5. Conclusion

The capacitance regeneration phenomenon usually occurs when the supercapacitor is used intermittently. The capacitance regeneration can prolong the lifetime of supercapacitor to a certain extent, but it can also affect the lifetime prediction of supercapacitor. In this paper, the first part is the experimental investigation of capacitance regeneration characteristics, the second part is the aging trend prediction of supercapacitor taking into account the capacitance regeneration. The results are as follow.

Increasing the charging voltage of supercapacitors, the amplitude of the capacitance regeneration decreases, and the amplitude of the capacitance regeneration also decrease gradually with the deepening of aging degree. The reason is that at high voltage the impurities produced by electrolyte
decomposition deposit on the electrode surface, and occupy the porous of the electrode surface, thus hindering the redistribution of charge. Temperature has little effect on the amplitude of capacitance regeneration. However, with the increase of temperature the recovery time of the regeneration capacitance becomes longer. The reason is that the thermodynamic movement of the charge is intensified at high temperature. The regeneration capacitance of supercapacitors decays faster than its inherent capacitance under the same aging test conditions. Taking into account the capacitance regeneration characterization, the aging trend prediction of supercapacitor is finished by using the SVM method, the prediction results are basically identical with the experimental results, and the RMS error range of the prediction is from 0.019 to 0.046.

6. References

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