A Modified Exponential Equivalent Parallel Resistance (EPR) Model for Predicting Self-Discharge Behavior of Printed Flexible Supercapacitors

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Abstract— **Typically, batteries are used to power interconnected Internet of Things (IoT) devices. Intermittent manual replacement of batteries or recharging them after complete depletion is one of their major disadvantages, which increases the cost of maintaining and restricts the large-scale use of devices. Considering the longevity of devices and battery limitations, and in order to achieve the integrated and efficient operation of IoT devices, the development of alternative power sources and power management strategies is inevitable. The supercapacitor is a suitable energy storage option for energy-harvesting powered autonomous wireless sensor nodes in IoT applications. The leakage current value provided for the supercapacitors by the manufacturers is tested after the supercapacitor has been floated at a constant voltage for a long time. This raises concerns about the uncertainty of dynamic leakage current behavior during repeated charging and discharging of the supercapacitor in IoT applications. At present, there is no effective method to estimate and predict leakage current and the discharging behavior of supercapacitors in IoT applications with the aim of achieving optimal performance. In this work, an improved simplified exponential model is presented in order to simulate the non-linear discharge behavior of our fabricated printed flexible supercapacitors in long-term (31 days). The printed supercapacitors are disposable and have been fabricated using low-cost and non-toxic processes and materials. The model proposed in this work is very well adapted to the experimentally measured self-discharge results of the supercapacitors. In addition, according to the experimental and data fitting results of 10 fabricated supercapacitors, all the parameters defined in this model show good statistical values and have a Gaussian (normal) distribution.**

Keywords—supercapacitors, printed supercapacitors, energy storage, self-discharge, leakage current, supercapacitor modeling, supercapacitor simulation, equivalent parallel resistance, EPR model, VLR model

I. INTRODUCTION

Over the past two decades, supercapacitors (SCs) also called electric double layer capacitors (EDLCs), have received intensive study as a potential form of energy storage [1]. A SC consists of two electrodes with porous microstructures , separated by an electrolyte and separator layer [2]. As compared to conventional capacitors, SCs are larger in capacitance value and have a greater energy density. In addition to their higher power density and higher charge/discharge efficiency, SCs have a shorter charging time and a longer cycle life compared to batteries, making them ideal for a large number of applications [3,4]. In a variety of applications, SCs can handle fast fluctuations in the energy level [5] and be employed both as auxiliary energy storage devices and as a primary power source [6]. It has been proposed that SCs can be used as energy storage systems in a wide variety of industrial applications including energy autonomous self-powered wireless sensor networks (WSNs), Internet of Things (IoT) and flexible and wearable electronic devices [7-9]. Moreover, an innovative energy storage textile was recently developed using graphene and manganese oxide as part of a flexible SC [10]. The fabric based SCs that are generated exhibit high specific capacitance, excellent electric conductivity, high flexibility, and a long cycle life [10].

Self-discharge and leakage current have been identified as a limiting factor for the practical application of SCs [11]. A self-discharge occurs when a SC is left in open circuit, in which the voltage of the SC spontaneously decreases with an effectively infinite external resistance. The effects of the self-discharge cannot be ignored, since they also have a considerable effect on SC's dynamic during rest periods, which can be disruptive to its function and may result in the loss of stored energy [12]. Three different main processes result in self-discharge, including Ohmic leakage, charge redistribution, and Faradaic reactions [13]. Almost certainly, Faradaic reactions are the dominant cause of the self-discharge phenomenon in SCs [14]. On the other hand, SC's leakage current refers to the tiny current that flows while the rated voltage continues to be applied to the capacitor [15]. The leakage current eventually becomes stable over time as it diminishes. Considering the detrimental effects of the self-discharge and leakage current, it is necessary to consider these characteristics when designing an electronic circuit with a SC. However, self-discharge and leakage current appear to have received less attention in the literature.

Various approaches for modeling the self-discharge in SCs have been reported in previous studies. A good modeling of this phenomenon enables us to obtain a reasonable estimate of the amount of available energy in the SCs at any given time. Earlier studies demonstrated that the SC dynamics can be physically described by various equivalent circuit models, such as classical [16], two-branch [17], multi-branch [18], ladder circuit models [19], etc. Based on equivalent circuit models, series and parallel resistances and capacitances are typically used to represent the resistance of porous carbon electrodes and the capacitance of carbon electrodes and electrolyte, respectively [20]. Models with two and three branches are more widely discussed in the literature. In order to take leakage current into account, a resistance branch is generally considered to be parallel to the other branches [21]. In some earlier publications [16], self-discharge/leakage current is modeled using a constant series or in-parallel resistance that is connected to an ideal capacitor (classical model). However, simply considering a constant resistance in classical model is not sufficient to simulate the self-discharge process over the long-term. In some other works [21], an equivalent circuit model based on variable leakage resistances (VLRs) has been proposed as a means of effectively describing the self-discharge effects of SCs. In these models, self-discharge is represented by a VLR parallel to the equivalent capacitance. VLRs can illustrate the dynamic charge leakage mechanism within SCs during the rest period. Moreover, there have been some studies in the literature on polynomial equivalent circuit models that incorporate VLR as a function of the terminal voltage [22]. Various time constants are present in these models during different self-discharge time and voltage intervals. In consequence, these models also contain several exponential functions and leakage resistances. The parameters of such models for long-term simulations would, however, be subject to a great number of exponential functions for a wide range of voltages and time periods, which would result in a huge number of parameter determination steps. Furthermore, it would be even more difficult to identify the parameters if the equivalent circuit model included multiple VLRs in SC energy modules in which a number of SCs are connected in series or in parallel. Besides, identifying the parameters of the dynamic polynomial function under a variety of experimental conditions will be quite challenging. In summary, the two-branch model with EPR, the three-branch model and the VLR models described in the literature have multiple branches and many RC network elements, whereas in practical applications, simplified versions are necessary to facilitate model implementation.

II. Experimental, Methods and Statistical

A. Experimental

The printed SCs used to develop this model were fabricated by this group. The fabrication process steps and characterization of the printed SCs have been described in earlier works published by the authors [14,23]. For the purpose of determining the EPR exponential factors corresponding to the self-discharge, all SCs were charged to a voltage of around 1.0 V and were kept at this voltage for 24 hours. Having been fully charged, the SCs were disconnected from the power source and their potential difference was monitored and measured for 31 days. As the rate of the self-discharge is higher at the beginning and in the early days, more data were collected in this period.

B. Method

As discussed in the introduction, equivalent circuit models reported in the literature have proven ineffective for long-term applications due to inadequate consideration of leakage and self-discharge effects. In this study, a simple model is proposed to overcome this limitation, which models the nonlinearity of leakage and self-discharge in the long-term. For each SC in the proposed equivalent circuit model, a conventional capacitor is used to model capacitance value, a series resistor to model ESR and ohmic losses, and a variable exponential equivalent parallel resistor (EPR) to model self-discharge and leakage current. This model has the same elements as the model that we reported in our earlier paper [23], although the exponential equation used for EPR and the method of obtaining EPR parameters differ from the previous paper. The current work uses $I=V\times e^{-(a+b\times V)}$ as the exponential equation of EPR representing self-discharge and leakage current effects, which actually exhibits a better fit with self-discharge experimental data. In addition, this exponential equation shows better suitability for Monte-Carlo simulations, which will be the focus of the authors' next research work.

We use the capacitor's discharge potential difference formula in order to obtain the EPR equation.

$$V=V_0\times e^{(-t/R\times C)},\ R=-t/(C\times ln(V/V0)) \tag{1}$$

The capacitance value 'C' has already been determined by the characterization of the printed SCs using the standard Maccor system [23,24]. On the other hand, based on the self-discharge experimental data of the SCs, we have already determined 'V0' as the initial potential difference, 't' as time and 'V' as the potential difference for each SC at a specific time. Therefore, the numerical value of the dynamic resistance can now be calculated for each data point and the resistance curve (R(V)) can then be plotted as a function of potential difference. On the subsequent step, we fit the exponential equation $e^{(a+b\times V)}$ to the R(V) data points. As a result, we can determine 'a' and 'b' parameters for each individual SC in this manner. For example, as illustrated in Fig. 1, for a SC, the R(V) experimental data points are fitted to the desired exponential function. According to the table in Fig. 1, the statistical fitting parameters for this fit, such as the R-square (COD) and Adj. R-square are very close to 1, indicating that the exponential fitting curve has a good fit with the experimental data points.

In order to be able to model the self-discharge and leakage of SCs, the leakage current for the SC must be defined as a function of the potential difference. As $R=V/I=e^{(a+b\times V)}$, hence $I=V\times e^{-(a+b\times V)}$ and this provides the SC's EPR for the proposed model. The equivalent circuit model of a SC presented in this work can be seen in Fig. 2.

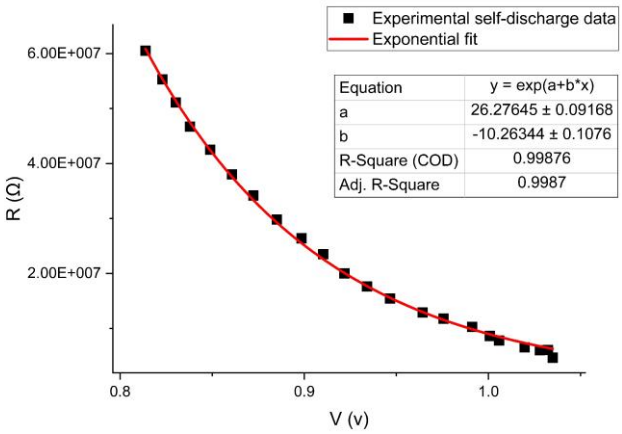

Figure 1. Exponential curve fitting of R(V) for a SC.

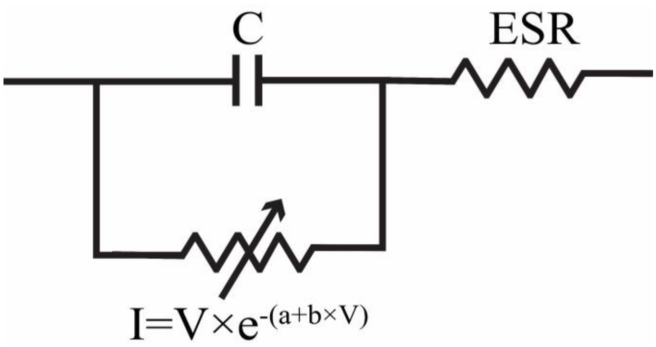

Figure 2. Proposed equivalent circuit model for a SC.

C. Statistical Tests of the Parameters

In order to develop the proposed model in this study, the characterization parameters ('C' and 'ESR'), self-discharge data, and EPR parameters ('a' and 'b') of 10 printed SCs were analyzed. The normal distribution (Gaussian distribution) was used to analyze the distribution of 10 SC parameters used in the development of the proposed model. Fig. 3 illustrates the histogram chart of all four parameters of the model; the distribution and the Bell curve (blue curve) for each parameter are included in the figure.

Furthermore, a normality test was conducted on every parameter to evaluate whether the data set for each parameter can be well described by a normal distribution. The following table summarizes the descriptive statistics for each parameter based on the normality test. According to table 1, the descriptive statistics indicate that all four parameters of the model are normally distributed. P-value and the approximate equality of mean and median values for each of the four parameters indicate a positive result for the normality test and prove that the normality test has been passed for each of the parameters. Moreover, these statistical values have demonstrated promising adaptability to Monte Carlo simulations.

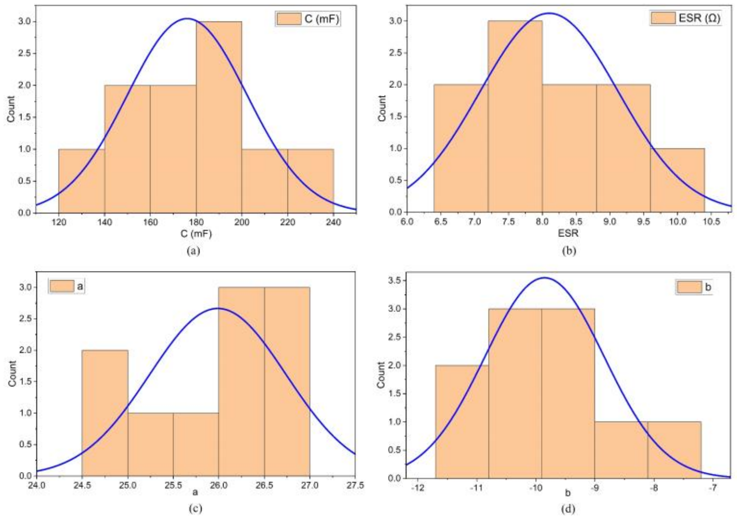

Figure 3. Histogram chart and Bell curve (normal distribution curve) for each parameter of the proposed model.

TABLE 1. DESCRIPTIVE STATISTICS FOR EACH OF THE FOUR SC'S PARAMETERS OF THE PROPOSED MODEL.

Parameters	C	ESR	a	b
N total	10	10	10	10
Mean	176.1	8.1	26	-9.9
Standard Deviation	26.2	1.0	0.75	1.0
Minimum	130	6.8	24.8	-11.6
Median	179.2	8.1	26.1	-9.9
Maximum	222.2	9.9	26.9	-8.0
p-value	0.98	0.62	0.36	1.0

III. RESULTS AND DISCUSSION

A. Accuracy of the proposed model in the self-discharge mode

For the purpose of evaluating the accuracy of the proposed model, the simulation results of the potential difference for four SCs in self-discharge mode were compared with experimental data collected for a period of 31 days. As can be seen in Fig. 4, there is no big difference between the experimental data and simulation results and a reasonable agreement can be observed between the simulation curve and the experimental data. After a period of 31 days, the difference between the measured experimental data and the simulation results is very small and the estimation error is less than two percent using the model presented in this paper.

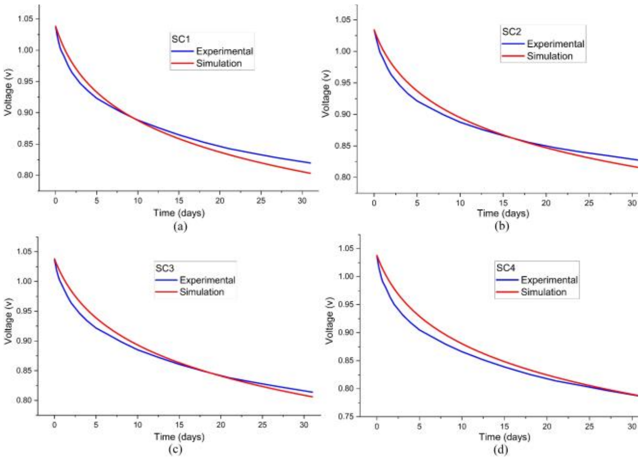

Figure 4. Experimental data and simulation results of the potential difference in self-discharge mode for four SCs over 31 days.

B. Long-term Self-Discharge Behavior Simulation of SC Energy Modules.

The printed SCs contain aqueous electrolytes, and because of the electrolytic window limitation, approximately 1.2 volts is the maximum voltage to which an individual SC can be charged [25]. Thus, for applications that require additional voltage, a SC energy storage module comprising a series connection of SCs will be needed. Our energy storage module is modeled by connecting three SCs in series. Charge and discharge circuits of an SC energy module consisting of three SCs connected in series are illustrated in [23]. We modeled three different energy storage modules using nine printed SCs. As can be seen in Fig. 5, the self-discharge behavior of different SC energy modules over the long term is simulated and compared. The simulation will enable us to estimate how much voltage each module will have at a specific time within 31 days. The final voltage of each module can also be predicted at the end of this period; based on that assessment, we can select the most appropriate module for our long-term application.

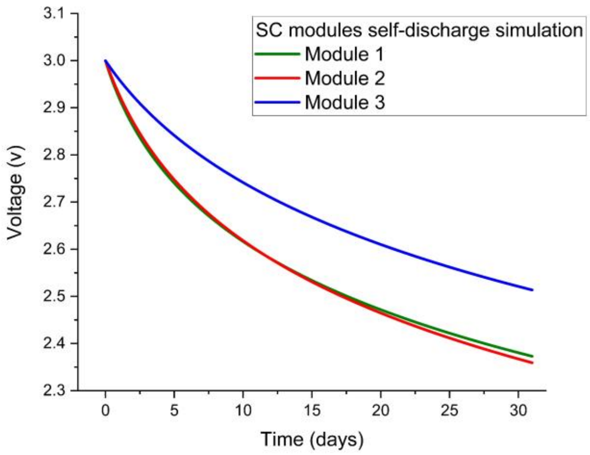

Figure 5. Simulation of the self-discharge behavior of three different SC energy storage modules over the long term. Each module consists of three SCs connected in series.

C. Accuracy of the proposed model in the load-connected mode

Furthermore, as a second experiment to verify the proposed model, the experimental and simulated results were compared in the context of a resistive load applied to SCs. This was accomplished by using discrete resistors as the resistance load connected to an SC energy module consisting of three SCs in series. In this experiment, the SC module was first charged up to 3 volts before a discrete resistor was connected to it. Using a digital multimeter, the voltage across the two ends of the discrete resistor was measured during discharge of the SC module. This experiment was repeated for three different discrete resistors and the experimental results were compared with the simulation results. As illustrated in Fig. 6, the differences between simulation and experimental results are negligible. In view of the results of this experiment and the previous experiment, it is evident that the proposed model can be considered well-validated in comparison with the experimental data.

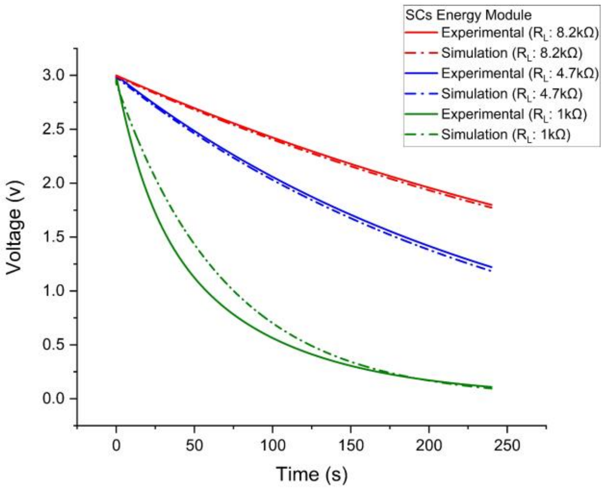

Figure 6. Verification of the proposed model accuracy against experiments using discrete resistors as resistive loads. Experimental and simulation behavior of an SC energy module.

IV. CONCLUSION

This paper presents a simple model in order to describe the dynamic self-discharge effects of printed supercapacitors. In order to model the non-linear behavior of self-discharge and leakage over the long term (31 days), a single exponential equation has been employed as the equivalent parallel resistance (EPR). On the basis of experimental results, it has been demonstrated that the proposed model is highly accurate for predicting the discharge behavior of printed supercapacitors in both self-discharge and load-connected modes. However, while the models reported in the literature have more RC network elements and branches, some of them have several separate exponential functions and also face difficulties determining the parameters, even in the short-term and are not accurate to simulate the long-term nonlinear self-discharge effect of the supercapacitors. Due to the need for simple versions for practical implementation, the model presented in this paper is more suitable for practical applications. Furthermore, the presented model can also be used to predict significant issues in the fabrication process of devices, as well as the behavior of a supercapacitor energy storage module depending on varying electrical variables from device to device. In addition, according to the experimental and data fitting results of 10 fabricated supercapacitors, all the parameters defined in this model show good statistical values and have a Gaussian (normal) distribution. Therefore, this model exhibits good compatibility with Monte Carlo simulations, which is going to be part of our upcoming plans to simulate the supercapacitor's charge and discharge behavior.

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