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Simplified exponential equivalent circuit models for prediction of printed supercapacitor's discharge behavior - Simulations and experiments

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HIGHLIGHTS

- A simple numerical exponential method to model supercapacitors' discharge behavior.
- Using experimental electrical parameters of supercapacitors to model self-discharge.
- Accurately modeling inherent non-linearity of self-discharge and leakage current.
- High accuracy prediction of long-term discharge behavior of supercapacitor modules.
- A practical approach to simulate supercapacitors' behavior based on only C and ESR.

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ABSTRACT

Although supercapacitors (SCs) are promising devices for energy storage systems due to their high-power density and long lifecycle, they suffer from high leakage current and self-discharge. In this work, a simple and practical exponential equivalent circuit model (ECM) and three sub-ECMs based on electrical parameters and self-discharge profile of 12 printed flexible SCs are proposed to account for non-linear leakage and self-discharge phenomena in SCs. The capacitance and equivalent series resistance (ESR) of SCs are determined from the experiments. Besides, rather than modelling different self-discharge mechanisms within a SC cell, an exponential current/voltage function is employed for each SC in this study as a variable leakage resistance (VLR). The proposed ECMs are based on empirical parameters, without considering the physical mechanisms. Using the ECMs and only knowing two to four parameters for each SC cell, the discharge behaviors of SCs, electrochemical double-layer capacitors (EDLCs) type may be predicted with a high degree of accuracy over the long term (maximum simulation error in 31 days: less than 4%). Accordingly, the proposed ECMs, in contrast to those published in the literature, have the potential to be used in practical applications in the long-term as a result of their simplicity and high accuracy.

1. Introduction

Due to the depletion of fossil fuels such as oil and natural gas, and the results of their CO_2 emissions, research into renewable sources of energy has increased significantly [1]. It is necessary to employ energy storage devices for optimum utilization of renewable energies since the captured form of resources may not always be available [2]. Energy storage systems are used as energy buffers to store the power harvested from energy sources like solar [3], radio frequency [4], mechanical vibration [5], human-body [6], and wind [7] and deliver the power to the system when needed. These systems play a key role in a wide variety of industrial applications such as energy autonomous Internet of Things (IoT) [8], energy-harvesting wireless sensor networks (WSNs) [9] and self-powered flexible and wearable electronic devices [10]. In choosing an energy storage system, power and energy density, safety, reliability, and longevity are the criteria that must be considered [11,12]. Rechargeable batteries such as NiMH [13] and Li-ion [14] have been widely used as primary energy storage devices due to their high energy density and low self-discharge. However, gradual increase in internal resistance and decrease in capacity over time because of the aging process of batteries during charge-discharge cycles, limits the lifetime of many applications [15]. Besides, due to their low power density, there is

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a possibility of disruption in their ability to deliver power under high current loads [16]. In addition, high current rates and transient load conditions severely affect the cycle life of rechargeable batteries [16]. Therefore, due to the limitation of the cycle life, it may be necessary to replace the batteries in applications after 1–2 years [16].

On the other hand, supercapacitors (SCs) also known as electric double-layer capacitors (EDLCs), have an energy density several orders of magnitude higher compared to conventional capacitors and despite having relatively low energy density compared to batteries, are a promising alternative to use in energy storage systems technology [17]. Essentially, a SC is composed of two electrodes with a large surface area and an electrolyte layer between them [18]. Charges are stored in SCs through these double layers at the interface between the active electrode and the electrolyte and thus, SCs are able to store a greater amount of energy than conventional capacitors [19]. In contrast to batteries, SCs have higher power density and charge-discharge efficiency, and lower internal resistance [18,19]. Furthermore, SCs benefit from fast charge-discharge characteristics [20], operation in a wide temperature range [21], longer cycle life, and recyclability [22]. In view of these advantages, they are suitable for use in a wide variety of applications, including uninterrupted power supplies [23], quick start, peak pulse power, fast charge, and memory backup applications, etc. [24–26]. In order to achieve "perpetual lifetime" in applications such as energy autonomous self-powered WSNs, IoT and wearable electronics, in some works reported in the literature, SCs have been used individually for storing the harvested energy [27] and in some other works, in combination with rechargeable batteries [28].

In spite of all this, SCs suffer from high leakage current, which limits some of their practical applications [29]. The self-discharge or leakage of a SC is the result of the inability of the SC to retain stored charge for a prolonged period of time. It is crucial to take self-discharge into account when determining the long-term performance of a SC and estimating the amount of energy available at any given time, such as in the case of power supply to WSNs, IoT, and wearable electronic devices. Despite the high importance of the self-discharge phenomenon and leakage current, SCs still remain largely unexplored in terms of these characteristics and thus far, a small number of studies have addressed the self-discharge mechanisms in SCs [30,31]. Mechanism of self-discharge in SCs is complicated due to the involvement of ions as well as a variety of electrode structures and contrary to conventional capacitors, cannot be explained solely by leakage resistance [32]. In addition, a number of material properties, including the structure and porosity of the electrode, presence of the impurities, ionic size of the electrolyte, accessible surface area etc., can also influence the self-discharge process [33]. However, the process of self-discharge is primarily attributed to three different mechanisms: charge redistribution, internal ohmic leakage, and diffusion-controlled Faradaic redox reactions [34]. Charge redistribution arises from differences in the accessibility of electrolyte ions to the electrode surfaces [34]. For the normal operation of the SCs, Faradaic redox reactions and internal ohmic leakage must be considered since charge redistribution can only occur if the cells are overcharged. The Faradaic redox reactions dominate the self-discharge during the first few hours while the internal ohmic leakage usually dominates the self-discharge during the rest of the open-circuit period [35]. Besides, leakage current in SCs is primarily caused by Faradaic redox reactions at the electrode-electrolyte interface [34,35].

In order to maximize the potential benefits of SCs in energy storage systems, understanding their electrical behavior is important. Moreover, since SCs are being used in a wide variety of applications, it is essential to have a simple model that represents their behavior in practical applications. Besides, as fast self-discharge causes charge/energy loss and voltage drop in SCs, it is necessary to understand the dynamic behavior of self-discharge in long-term and develop an accurate terminal voltage prediction model in order to optimally design power management systems and find the best system architectures. This can be achieved through the equivalent circuit model (ECM) of a SC, which is an easy, simple, and accurate method in contrast to the other models such as electrochemical models, which require high computational complexity [36]. Additionally, the ECM can also be used as an important tool to reveal the nonlinear behavior of charging and discharging in SCs, as well as the redistribution of charges and self-discharge processes before deploying SCs in practical applications. In the literature, various ECMs for SCs have been developed recently. The reported ECMs differ in representing the implementation of SCs in different applications, and for specific applications, specific ECMs are proposed. In some reports of modeling SCs through ECM and analyses in the time [37] or frequency domain [38], diverse resistive-capacitive (RC) networks are used. In the last work published by this group [39], several ECMs for SCs reported in the literature were reviewed. In this paper, we now refer to the ECMs that have been published in recent years.

SCs have been modeled using a two-branch approach (Fig. 1a) in some publications [40,41]. In these ECMs, in order to account for leakage current and self-discharge, a couple of parallel branches of constant RC networks were added. In accordance with the self-discharge behavior, circuit elements were determined experimentally. Nevertheless, based on the constant parallel resistance used in this ECM, only the internal ohmic leakage of the SC is considered. As a result, modeling the leakage and self-discharge with constant RC elements may not be accurate, due to their non-linear inherent nature. This leads to a large difference between simulation and experimental results over long times. Additionally, some other studies have reported an ECM with two RC branches and a variable leakage resistance (VLR) [37,42], as can be seen in Fig. 1b. In these ECMs, the two RC branches have different time constants, which characterize the charging-redistribution process, and the VLR characterizes the self-discharge process. There are several different exponential functions in the VLR used in this ECM to model the self-discharge characteristic, each of which has a different time constant at various voltages and times, resulting in varying leakage resistances. Nevertheless, a huge number of distinct exponential functions must be determined for many periods in order to analyze and study the SC's self-discharge behavior over the long-term using these VLR ECMs. Another publication [43] modeled a SC by adding a controlled current source to the two-branched ECM (Fig. 1c). In this improved two branch ECM, based on the terminal voltage of the SC and its change rate, the controlled current source was designed. This ECM with the controlled current source is suitable for middle-term simulation of SC behavior (less than 30 min). Nonetheless, firstly this ECM is still complex, requiring numerous parameter determination steps, and secondly, it is not suitable for long-term simulations. In other publications [35,44], researchers reported an ECM in which three RC branches and an additional equivalent parallel resistor (EPR) to consider the self-discharge phenomenon are connected in parallel (Fig. 1d). In these ECMs, the largest capacitor does not have a constant value and instead has a linear relationship with the voltage [35,44]. However, in spite of the complexity of the ECM and the increased number of RC network elements, a three-branch ECM is also not capable of accurately estimating the nonlinear self-discharge effect in SCs over the long-term. Furthermore, other researchers have also reported ECMs based on polynomial functions. In Ref. [45], Saha et al. presented a polynomial ECM for the self-discharge process dominated by charge redistribution in SCs. These polynomial ECMs also require numerous parameter determination steps, which makes them unsuitable for use in practice. A further challenge will also be the identification of the dynamic polynomial function parameters under a variety of experimental conditions in these ECMs. Moreover, a model of a SC with a blocking layer of a few nanometers in order to reduce the leakage effect was presented by Tevi et al. [46]. The blocking layer was modeled as a capacitor, connected in series with the main double-layer capacitor. Although their proposed ECM accurately predicts experimental data in the short term, no long-term simulation results have been reported. Besides, de Levie's transmission line model (TLM) has also been extensively used for modeling ions' short-term movement inside electric double-layer capacitors with porous

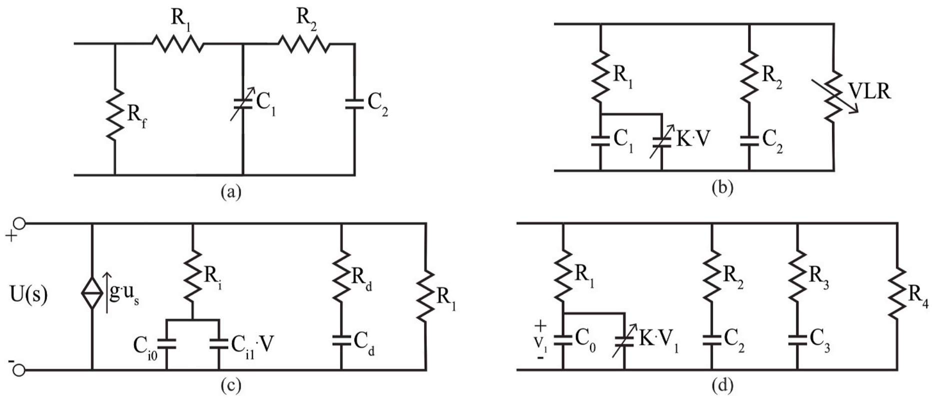


Fig. 1. ECMs for a single SC reported in the literature; a) Two-branch ECM [40,41]. b) Two-branch ECM with VLR [37,42]. c) Two-branch ECM with a controled current source [43]. d) Three-branch ECM with EPR [35,44].

electrodes [47].

A brief summary of the literature indicates that the reported different ECMs have multiple branches and more RC network elements, whereas in practical applications, simplified versions are required to facilitate the implementation of the ECMs. Besides, in order to form SC energy modules for the purposes of realizing energy storage systems and addressing the power requirements, several SCs need to be connected in series and/or parallel [48] into modules. Therefore, the reported ECMs are not suitable for long-term simulation in SC energy modules, as they would further increase the difficulty of parameter identification. Consequently, despite the complexity and the inclusion of more characterization steps, none of the ECMs reported in the literature adequately reflect the characteristics of the SCs in long-term, leading to inconsistent long-term results between simulations and experiments.

This work presents a simple numerical exponential method using experimental electrical parameters of printed SCs to model the non-linear behavior of self-discharge and leakage current in SCs, type of electrochemical double-layer capacitors (EDLCs). This proposed ECM is based on the previous model published by the authors [39,49], but the exponential function used in the EPR has now been modified and the method of obtaining EPR is also different than the previous works. This modified exponential function exhibits improved statistical parameters and is also compatible with Monte-Carlo simulations. This study simplifies the proposed ECM even further and proposes a super-simple ECM based on the numerical value of the capacitance solely to estimate the discharge and self-discharge behavior of SCs (EDLC type) over a prolonged period of time (31 days). This ECM contains only one branch and two RC elements, and since practical applications require simplified versions to facilitate model implementation, it is well suited for practical use. Accordingly, the presented ECM is simpler in comparison to the previous ECMs found in the literature and is therefore more suitable for use in energy storage modules containing several SCs integrated either in series or in parallel. The proposed ECM can also be used to predict how series-connected SC energy modules operate depending on the variation of electrical properties from device-to- device, which is a critical consideration in printed electronic devices. Thus, the reported super-simple ECM is not only capable of modeling the full charging and discharging behavior of SCs but can also be applied to analyzing how device-to-device variations in electrical parameters, such as the non-linear inherent of self-discharge and leakage current, affect the performance of series-connected SCs in energy modules.

Nonetheless, it should be noted that the proposed ECMs are based on empirical parameters without taking physical mechanisms into account and can only be used to predict the behavior of EDLC-type SCs. The ECMs reported in this work may not be necessarily applicable to the other types of SCs such as pseudo-capacitors or hybrids (combination of EDLCs and pseudo-capacitors). Furthermore, in order to gain an understanding of the mechanisms underlying the performance and aging of SCs, additional characterizations will be required.

2. Experimental and methods

2.1. Experimental

Printed SCs of the type of electrochemical double layer capacitors (EDLCs) are used in building the model presented in this paper and verifying the simulation results. Previous publications by the group have described in detail the process of fabricating these types of printed SCs [39,50–52]. However, the fabrication process is described in a very brief manner here. As a current collector, graphite ink was applied to the PET side of a double-sided flexible Al-PET substrate, while the Al layer serves only as a barrier. On the current collector layer, activated carbon ink was applied using an in-house formulation with chitosan as a binder to form an electrode layer. These two layers were deposited using a laboratory-scale doctor blade coater. On top of the electrode layer, NaCl: H_2O aqueous electrolyte was added, followed by a paper separator. In the final step of the process, an annealed adhesive material was used to heat-seal two electrodes face-to-face to form a SC.

We have also previously reported the characterization process for printed SCs using a Maccor workstation (Maccor Inc., USA) by which the key electrical parameters are obtained [39,50–52]. This process is, however, also summarized here. Three times of charging and discharging of SCs were conducted between 0 and 1.2 V with a constant current of 1, 3, and 10 mA. Following this, the SCs were maintained at 1.2 V for 30 min at constant voltage. Using a constant current discharge step between 0.96 V and 0.48 V, the capacitance was measured. A constant voltage of 1.2 V was then applied to the SCs for 1 h in order to determine the leakage current. The procedure was repeated for all three currents of 1, 3, and 10 mA. In the end, the ESR was calculated based on the IR drop in the measurement with a discharge current of 10 mA. In the supplementary material file, the characterization results for all SCs used to develop the model are provided. Among the electrical parameters of the SCs, capacitance (C) and equivalent series resistance (ESR) will be utilized in the model. The model is based on the characterization results of 12 printed SCs. After fabrication and characterization, each of the 12 SCs was charged up to approximately 1 V and then maintained at this constant voltage for 12 h (charging time: 12 h). The SCs were disconnected from the power source after charging and the potential difference data for each SC were monitored and recorded for 31 days during self-discharge.

2.2. Model

In order to model the internal parameters of a single SC in this study, a conventional capacitor (C), an equivalent series resistor (ESR), and a parallel variable exponential element as EPR (equivalent parallel resistor) are used as illustrated in Fig. 2a. As mentioned above, the 'C' and 'ESR' values are determined using standard characterization. ESR represents the internal Ohmic losses of a SC caused by the combined effect of the current collector resistance, electrode contact resistance, electrolyte resistance, and the electrode/electrolyte interface resistance [53]. The variable exponential EPR models the nonlinearity of SC self-discharge and leakage current. In some respects, the proposed model is similar to the work published by the authors earlier; however, the exponential EPR function used in this model and the method for obtaining this element are different. This work uses $I = e^{(a+\, b\times V)}$ as the exponential equation of EPR describing self-discharge and leakage current effects, which provides a better fit to the empirical data for self-discharge. This exponential equation has also the advantage of being suitable for Monte-Carlo simulations due to the normal distribution of the parameters in this equation.

2.3. Method

In this paper, a simple model is proposed to model the nonlinearity of leakage and self-discharge in the long-term (Fig. 2a). As discussed in the experimental section, the experimental self-discharge potential difference (voltage) data of each SC over time have been recorded to determine the exponential function of EPR. Using capacitance and current basic formulas (1), we can now calculate numerical values of the current (2) at any given voltage for each SC based on capacitance (C) and self-discharge. As can been seen in formula (2) and Fig. 2b, in order to determine the current at each data point, the difference between the values of that data and the previous data is used.

$$Q = C \times V,\ I = dQ/dt \tag{1}$$

$$I_m = C \times dV_m/dt_m = C \times (V_{m-1}-V_m)/(t_m-t_{m-1}) \tag{2}$$

With the current data-points calculated, we are now able to plot the diagram of the I (V) data-points for each SC as shown in Fig. 2c and . d. In the following step, we fit the exponential equation $e^{(a+\, b\times V)}$ to the I (V) data points of each SC and as can be seen in Fig. 2c and d, SC's parameters 'a' and 'b' for two SCs are uniquely determined by fitting this exponential function. As a result of this exponential function, excellent statistical data fitting parameters, such as the R-square and Adj. R-square values, are evident. R-square, also referred to as coefficient of determination (COD), is a measure of how much variation in the response variable is explained by the fitted regression line. As a general rule, the closer the R-square is to 1, the better the fitted line would track the data. Accordingly, the fit line will explain all the variability around its mean if R-square is one. All 12 SCs in this study exhibit R-square values exceeding 0.99 using this exponential function, which shows excellent fit to the I (V) datapoints for all SCs. Based on this exponential function fit, we are now able to determine the numerical values of 'a' and 'b', parameters of the model, which are unique to each SC. With these two parameters, as well as the characterization parameters 'C' and 'ESR', all four parameters of this model are now revealed. This model (Fig. 2a) will be referred to as ECM 1 throughout this article.

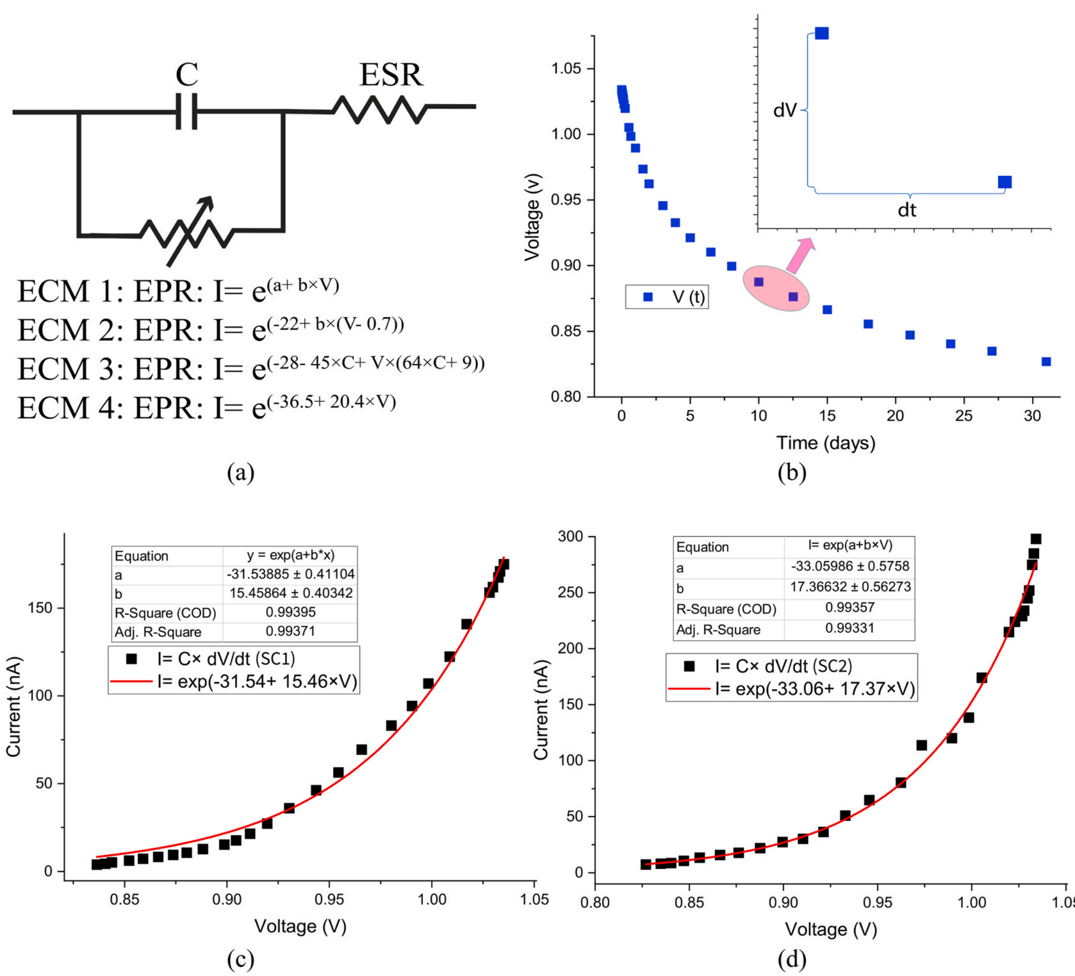


Fig. 2. a) Proposed ECMs for a single SC. b) Experimental self-discharge data of a SC. c) Fitting the exponential function to the I(V) datapoints of SC1. d) Fitting the exponential function to the I(V) datapoints of SC2.

2.3.1. Statistical study of parameters

In order to examine and analyze the distribution of each parameter in ECM 1 and assess whether the data set for each parameter can be adequately described by a normal distribution (Gaussian distribution), every parameter of this model is subjected to a normality test. Fig. 3 illustrates a histogram chart and normal probability plot for each of the four parameters in this model. In histogram charts (Fig. 3a, c, e, g), the distribution as well as the bell curve (blue line) for each parameter are included. Besides, it is also possible to evaluate substantive deviations from normality on the normal probability plots (Fig. 3b, d, f, h) by comparing data deviations from the reference line (red line); the closer the percentiles are to the reference line, the more normal the

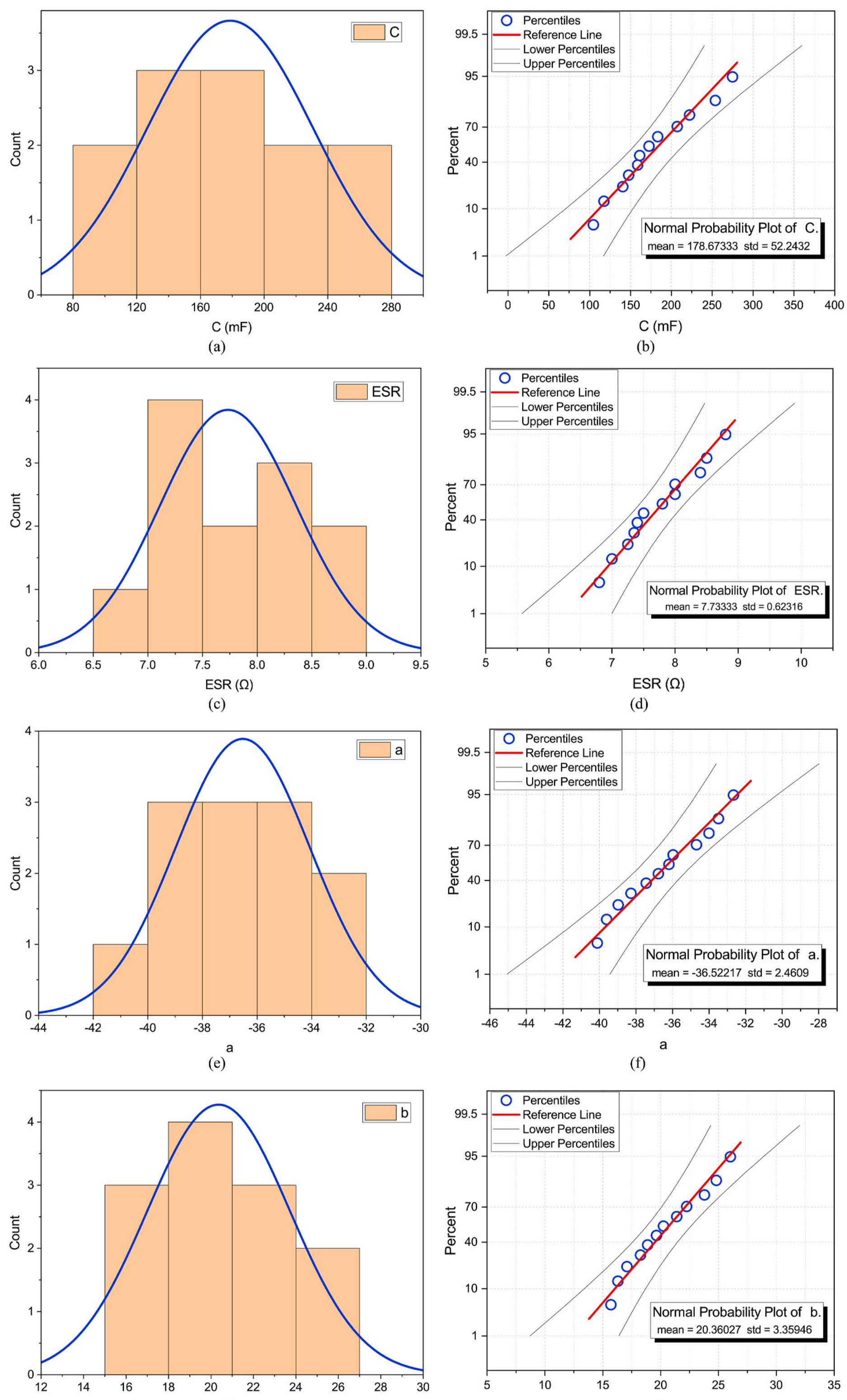


Fig. 3. a,c,e,g) Histogram chart of the ECM 1 parameters. b,d,f,h) Normal probabilty plot of the ECM 1 parameters.

distribution of the parameter appears. According to the normality test, Table 1 summarizes the descriptive statistics for each parameter. All four parameters of ECM 1 exhibit a normal distribution based on the numerical value of the descriptive statistics in Table 1. P-values for each of the four parameters are higher than 0.8, which strongly supports the normal distribution hypothesis. Besides, generally, a skewness value between −0.5 and 0.5 indicates that the probability distribution of a random variable is approximately symmetrical about its mean, as each parameter in ECM 1 is. Furthermore, since the mean and median values for each parameter in Table 1 are approximately equal, this indicates a positive result for the normality test and confirms that each parameter has passed the normality test. Additionally, the statistical values presented here have been found to be highly adaptable to Monte-Carlo simulations.

2.3.2. Simplifying ECM 1

As has already been discussed, ECM 1 presented in this work has four parameters (Fig. 2a). Compared to other models in the literature, this model is very simple and is well suited for long-term simulations, as discussed in the following section (section 3). As a result of its simplicity and accuracy, ECM 1 is already useful for practical applications. However, the objective is now to simplify the model even further since simpler models are easier to implement and more feasible to use in practical applications. Further simplifying this model requires reducing its parameters and for this, it is necessary to determine a relationship among the parameters in order to formulate the EPR exponential I(V) function based solely on one parameter. In Fig. 4a and b, it can be observed that 'C', 'a', and 'b', the parameters of ECM 1 for 12 printed SCs used in this model, exhibit a relatively good linear relationship. In order to obtain a good approximate representation of this relative linear relationship among the parameters, linear fits are used (Fig. 4a and b). It is worth mentioning that these two linear fits have R-square and Adj. R-square values (statistical data fitting parameters), above 0.97. Having defined the linear relationship among the parameters, the next step is to formulate the exponential equation for EPR based on only one parameter:

$$\text{EPR: } I = e^{(a + b\times V)},\ a = -0.7 \times b - 22 \rightarrow I = e^{(-22 + b\times(V - 0.7))} \text{:ECM 2} \quad (3)$$

$$b = 64 \times C + 9 \rightarrow I = e^{(-28 - 45\times C + V\times(64\times C + 9))} \text{:ECM 3} \quad (4)$$

The EPR exponential I(V) function has now been obtained once based on only parameter 'b' and once based on only parameter 'C'. During the following discussion in this paper, the ECM based on only parameter 'b' is referred to as ECM 2, and the ECM based on only parameter 'C' is referred to as ECM 3 (Fig. 2a). ECM 2 and ECM 3 are simpler than ECM 1, since they use three parameters rather than four.

An alternative approach to simplifying model 1 is also to replace the mean values of parameters 'a' and 'b' in the EPR exponential function. In this case, the EPR function would be $I = e^{(-36.5 + 20.4\times V)}$. This ECM is referred to as ECM 4 throughout this article (Fig. 2a). Compared with the previous ECMs in this paper, ECM 4 is extremely simple and straightforward, due to the advantage of having only two parameters ('C' and 'ESR') and not containing any parameters for the exponential EPR function.

Table 1
Descriptive statistics of ECM 1 parameters.

Parameters	C (mF)	ESR (Ω)	a	b
N total	12	12	12	12
Mean	178.7	7.7	−36.5	20.4
Minimum	104.4	6.8	−40.1	15.7
Median	167.0	7.6	−36.5	19.9
Maximum	274.9	8.8	−32.7	26.0
Std	52.2	0.6	2.5	3.4
P-value	0.83	0.86	0.9	0.91
Skewness	0.49	0.26	0.07	0.29

3. Results and discussion

3.1. Accuracy of the proposed ECMs

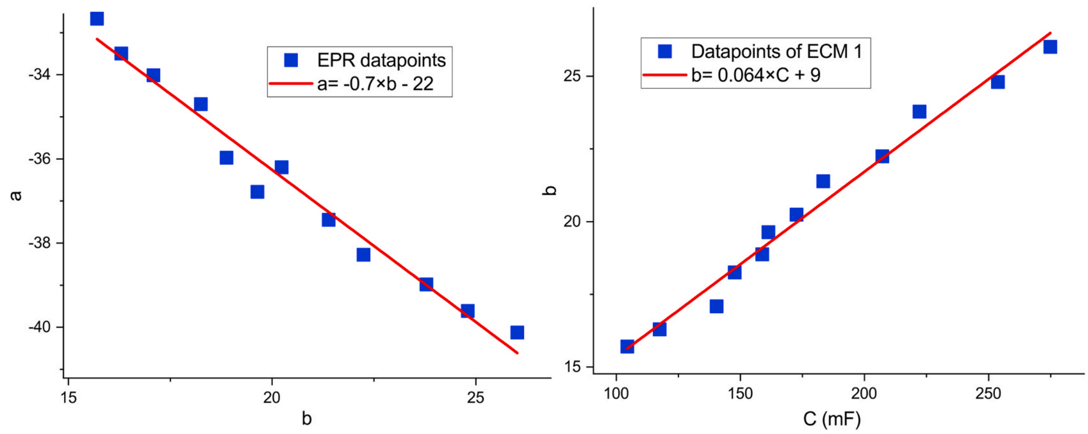
The accuracy of the proposed ECMs is evaluated in four different ways in this study. The first approach is to compare the simulation results with the experimental results of the SCs which were used to develop the ECMs. In the second approach, simulation, and experimental results of new SCs that were not used in the development of the ECMs are compared. The third accuracy test of the presented ECMs involves the comparison of experimental results with simulations of two commercially available SCs. Finally, in the fourth and last approach, two separate SC energy modules, each consisting of three SCs connected in series, are formed and each module is connected to a discrete resistor with different resistance values. Then, the amount of voltage delivered to the discrete resistor during the discharge of the SC module is compared with the simulation results.

3.1.1. SCs used to develop the ECMs: simulation results vs. experiments

Approach one for evaluating the accuracy of the proposed ECMs is as follows: A random selection of four SCs is made out of the 12 used to build the ECMs, and the simulation results based on different proposed ECMs in the self-discharge phase are compared to the experimental results. Fig. 5 illustrates both the potential difference graph of the SCs over time during self-discharge in the long-term (31 days) as well as the residual voltage graph over time (residual voltage = experiments – simulations). As shown in Fig. 5, the simulation results based on all ECMs are in good agreement with the experimental results over a period of 31 days. According to this figure, ECM 1, which includes four parameters ('C', 'ESR', 'a', and 'b') for a single SC, is extremely accurate; in fact, the maximum error in the self-discharge phase based on ECM 1 within 31-days is about 10 mV (Fig. 5d and f), which is roughly 1.2% of the SC's final voltage (the final voltage of SCs drops to about 0.8 V after 31 days of self-discharge). ECM 2 including three parameters for a single SC (EPR function in ECM 2 is based only on 'b') in the long term, has a maximum error of 21 mV (2.5%). However, ECM 3 and 4, which are the most simplified ECMs proposed in this work with only two parameters for each SC ('C' and 'ESR'), have a maximum error of around 33 mV (4%) (Figs. 5h) and 18 mV (2.2%) (Fig. 5d) respectively, in the long-term. Therefore, based on ECM 4 and by only knowing 'C' and 'ESR' values of a SC, its self-discharge behavior can be estimated with a very good approximation (2.2% error) over the long term (31 days). Table 2 summarizes the maximum simulation error based on each ECM, according to the self-discharge experimental and simulation results for these four random SCs.

3.1.2. SCs not used to develop the ECMs: simulation results vs. experiments

As a second way to verify the accuracy of the proposed ECMs, the ECMs are applied to new SCs that have not been used for the development of the ECMs. Towards this objective, the experimental results of the self-discharge behavior of four randomly selected SCs are compared with the simulation results based on the ECMs. In this study, to evaluate the comprehensiveness of the ECMs, both SCs similar to the previous ones used to build the ECMs and other SCs with different substrates have been used. All 12 SCs used in the development of the ECMs in this work are printed on Al/PET substrate, and SC1 and SC2 in this test are also printed on Al/PET substrate with the same fabrication process. SC3 and SC4 have different substrates (PET/PLA and Al/PLA, respectively), but the fabrication process is the same. As can be seen in Table 3, the capacitance values of SCs 1, 2, and 3 are within the range of the capacitances of SCs used in the development of the ECMs (104–275 mF), whereas the capacitance of SC 4 exceeds this range. In fact, these SCs are printed in different batches, which explains the difference in capacitance values. By using this fabrication process, eight SCs are printed in each batch, and since the doctor blade tool is adjusted to the same thickness in each batch, approximately the same amount of activated carbon ink will



(a) (b)

Fig. 4. a) A linear relationship with a good approximation between parameters 'a' and 'b' of ECM 1. b) A linear relationship with a good approximation between parameters 'b' and 'C' of ECM 1.

be printed on the graphite ink for all 16 SC cells, resulting in the almost same capacitance value for each SC (this process of fabricating SCs has been discussed in detail in Ref. [39]). Therefore, due to the thickness adjustment of the doctor blade tool, the different amount of activated carbon ink will be printed in different batches which will result in different capacitance values for the SCs. However, the ESR values of the selected SCs are all higher than those used in developing the ECMs (6.8–8.8 Ω). The selection of SCs with these values of capacitance and ESR has no particular purpose, and as mentioned all four SCs are selected at random.

Fig. 6 illustrates how well all the proposed ECMs work for the new SCs as well, and the self-discharge simulation and experimental results are in good agreement over the long-term (31 days). In addition, Table 3 provides a summary of the maximum simulation error for each ECM. According to this table, ECM 1 has a maximum error of 17.64 mV (2.21% of the SC's final voltage value) (Fig. 6e and 6f). The maximum error for ECM 2 is 26.49 mV (3.29%), for ECM 3 is 12.48 mV (1.56%), and for ECM 4 is 13.87 mV (1.74%). There is an interesting observation that ECMs 3 and 4, which are the simplest ECMs presented in this work, including only two parameters ('C' and 'ESR') for a single SC, are slightly more accurate than ECMs 1 and 2 with a maximum error of less than 2%, although the difference is within the experimental uncertainty. In other words, using proposed ECMs 3 and 4, one can predict the self-discharge behavior of a SC in the long term (31 days) with an error of less than 2% only by knowing the numerical value of capacitance and ESR. Considering the simplicity of the ECMs, it can be concluded that the maximum simulation error obtained for the new SCs based on all ECMs is negligible over the long term, and all ECMs have excellent accuracy.

3.1.3. *Verification using commercial SCs (EDLC type): simulation results vs. experiments*

As for the third part of the verification process of the proposed ECMs, self-discharge experimental results of two commercially available SCs, type of electrochemical double layer capacitors (EDLCs), are compared with the simulation results based on ECM 4. This ECM is the most simplified ECM in this study and by knowing only the capacitance and ESR value, the charge and discharge behavior of SCs can be simulated. The self-discharge experimental results for the two commercial SCs used in this test were obtained from the literature [54,55]. Commercial SC1 is a carbon-based SC with acetonitrile electrolyte and a capacitance of 600 F [54]. Commercial SC2 is also a carbon-based SC with organic electrolyte and a capacitance of 2600 F [55]. SC1 was charged up to 1.3 V and kept at that voltage for 24 h (charging time: 24 h) [54]. SC2 was charged up to 1.5 V with a charging time of 1 h [55]. After the charging process, the open circuit potential difference (self-discharge behavior) of SC1 and SC2 was monitored and recorded for 15 and 7 days, respectively [54,55]. Fig. 7a illustrates how closely the simulation results follow the experimental results for both SCs over time. The residual voltage over time for both SCs is also shown in Fig. 7b. As can be seen, the maximum simulation error for SC1 and SC2 is approximately 34 mV and 17 mV, respectively. Accordingly, the maximum simulation error for SC1 in 15 days is approximately 2.6% of the initial voltage and for SC2 in 7 days is 1.1% of the initial voltage, demonstrating that the proposed ECM is highly accurate for these two commercial SCs (EDLC type) as well.

As the printed SCs used in this study are of the EDLC type, commercial EDLC SCs are also used for verification. Therefore, the ECMs proposed in this work may not be applicable to other types of SCs such as pseudo-capacitors, and hybrid types formed by a combination of EDLCs and pseudo-capacitors.

3.1.4. *Verification using discrete load resistors: simulation results vs. experiments*

For an additional comparison of experimental results to the predictions of the model, discrete resistors in two different values (R_L:1.0 and 4.7 kΩ) are used to verify the accuracy of the proposed ECMs. First, two SC energy modules are formed, each consisting of three SCs connected in series using the 12 SCs used to develop the ECMs. Compared to module 1, the SCs of module 2 have a larger capacitance value difference. SC modules are first fully charged to a voltage of 3 V each and as soon as the energy module is fully charged, the main power source is disconnected. The discrete resistor is then used as the resistive load connected to the SC module and the voltage value between two ends of the discrete resistor during discharge of the SC module is measured using a digital multimeter. The ECM of the SC module and the resistive load is shown in Fig. 7c. In the ECM, the main 3V power source is connected to the module at $t = 0$, and the energy module is fully charged to 3 V. Each SC in the module is fully charged and stores the potential difference corresponding to its capacitance and then the main power source is disconnected at $t > 0$.

Fig. 7d, e, f, and g depict the discharge of the SC energy module. Fig. 7d and f illustrate the simulation and experimental results of the potential difference of the resistive load during the discharge of the SC module 1 and 2, respectively in the short-term (2 min) (In Ref. [39], the experimental results in Fig. 7d and f have already been published). According to these figures, the simulation results are consistent with the experimental results with a good degree of accuracy, and the difference between the simulations and experiments is small. In both modules, this difference is very close to zero for the resistive load of 4.7 kΩ. Fig. 7e and g shows the residual voltage for SC modules 1 and 2, which can be used to obtain the simulation error for each module by calculating the

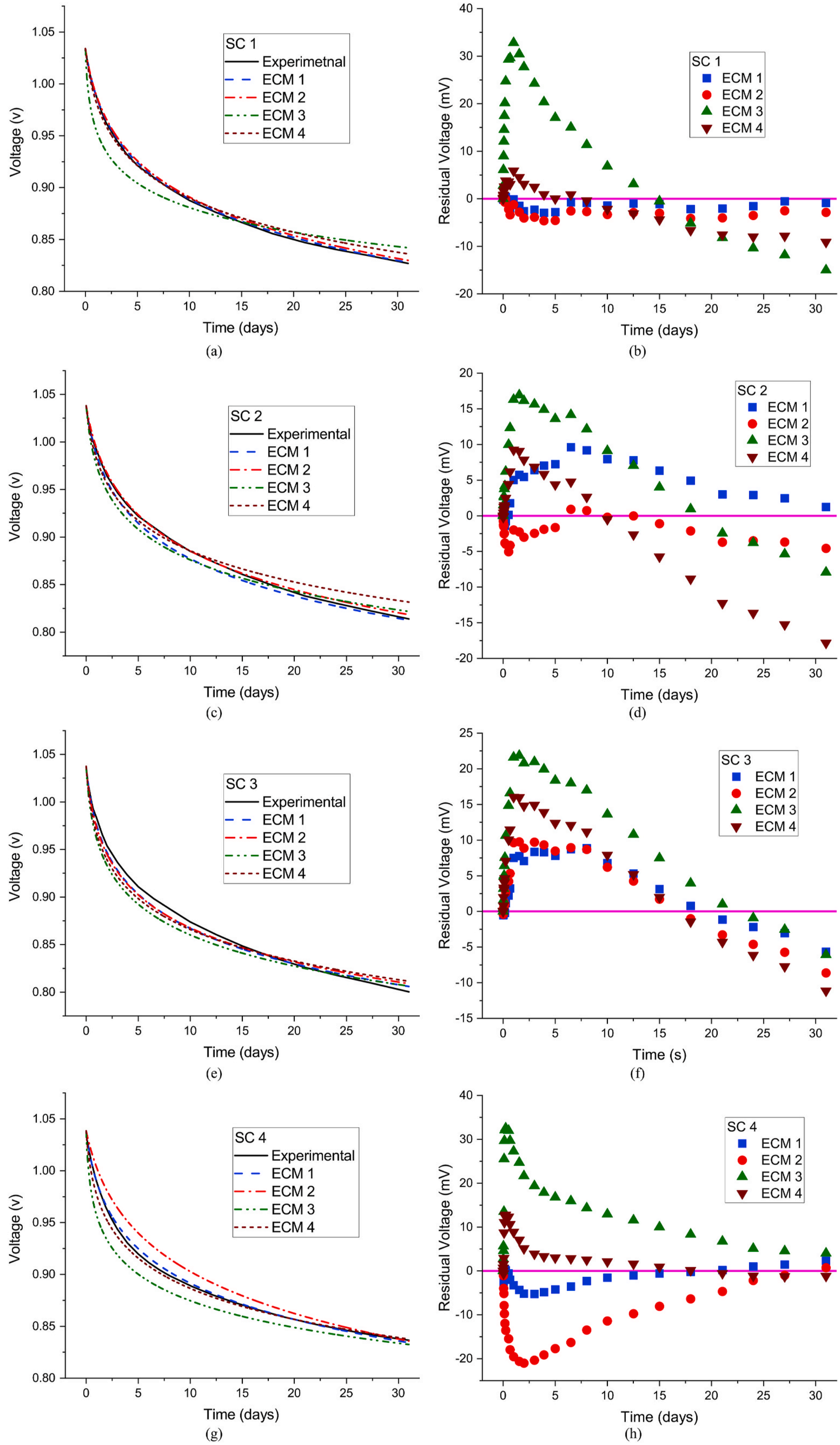


Fig. 5. a,c,e,g) Self-discharge experimental and simulation results in 31 days based on proposed ECMs for four randomly selected SCs used to develop the ECMs. b,d, f,h) Residual voltage (the difference between experiments and simulations).

Table 2
Maximum self-discharge simulation error in 31 days based on proposed ECMs for four randomly selected SCs used to develop the ECMs.

	SC 1	SC 2	SC 3	SC 4
ECM1	2.95 mV (0.36%)	9.6 mV (1.18%)	8.87 mV (1.11%)	5.26 mV (0.63%)
ECM2	4.61 mV (0.56%)	5.04 mV (0.62%)	9.76 mV (1.22%)	20.98 mV (2.51%)
ECM3	32.8 mV (3.97%)	16.93 mV (2.08%)	21.86 mV (2.73%)	32.54 mV (3.89%)
ECM4	9.1 mV (1.1%)	17.82 mV (2.19%)	16.04 mV (2%)	12.78 mV (1.53%)

Table 3
Maximum self-discharge simulation error in 31 days based on proposed ECMs for four randomly selected SCs not used to develop the ECMs.

	SC 1, (Al/PET)	SC 2 (Al/PET)	SC 3 (PET/PLAU)	SC 4 (Al/PLA)
C (mF)	126.4	211.2	157.7	326.5
ESR (Ω)	10.3	11	13	12.4
ECM 1	4.16 mV (0.5%)	13.8 mV (1.71%)	17.64 mV (2.21%)	2.53 mV (0.3%)
ECM 2	11.35 mV (1.37%)	26.49 mV (3.29%)	15.13 mV (1.89%)	14.53 mV (1.74%)
ECM 3	9.03 mV (1.09%)	10.46 mV (1.3%)	12.48 mV (1.56%)	1.81 mV (0.22%)
ECM 4	7.73 mV (0.94%)	11.38 mV (1.41%)	13.87 mV (1.74%)	12.59 mV (1.51%)

absolute value of this residual voltage over time. As a result, for the resistive load of 1 kΩ, the maximum simulation error for module 1 is 47 mV, for module 2 the error is 243 mV, corresponding to 1.57% and 8.1% of the module's initial voltage, respectively. In addition, an interesting aspect of these short-term simulations (2 min) is the full compliance among the simulation results based on ECMs 1 to 4, which implies that leakage and self-discharge do not play any significant role in the short term and have almost no influence in the initial minutes of SC discharge behavior. In contrast, the capacitance value of SCs is a more important factor in the discharge behavior of SCs over a short period of time. Consequently, it may therefore be argued that the higher simulation error of module 2 compared to module 1 can be caused by the larger difference in the capacitance value of its SCs.

All in all, based on the results of all methods of accuracy analysis, the estimation accuracy of all proposed ECMs can generally be assessed as acceptable in view of their simplicity.

3.2. Self-discharge behavior of SC modules: simulation results vs. experiments

The power that can be stored in a single SC may not be sufficient for some applications. Due to the limited potential window of SCs, it is not possible to store voltage beyond a certain limit, so the solution is to connect several SCs in series to form a SC energy module. Since the stored potential difference in a SC does not remain constant during its resting phase (open circuit) and decreases with time as a result of self-discharge, hence, in the long term, it is crucial to estimate the amount of power stored in the energy module that is available and ready to be delivered at any given time. Based on the ECMs presented in this work, it is now possible to predict the voltage over each SC energy module at any given time.

In this regard and as an illustration, four SC energy modules are formed, each consisting of three SCs connected in series based on the 12 SCs used to develop the ECMs. An ECM of this energy module in charge and discharge mode is already shown in Fig. 7. c, but in this case, there is no resistive load, and the module is at the rest phase (open circuit or self-discharge). Table 4 presents the parameters of the three SCs that form each module. As can be seen in this table, from module 1 to module 4, the difference in capacitance value among the SCs forming each module increases; accordingly, module 4 has the largest difference in the capacitance value of its SCs. Despite this, the total capacitance value of the modules is not significantly different. In addition to experimental results, Fig. 8 presents an estimation of the voltage still remaining in each of the four modules on the basis of the proposed ECMs over a period of 31 days.

According to experimental and simulation results, the voltage still remaining in module 4 on day 31 is lower than the voltage remaining in the other modules, as can be seen in Fig. 8 and Table 5. These results reveal that the larger the difference in capacitance value among the three SCs in a module, the lower the final voltage value still stored in the module will be in the long-term (self-discharge and leakage will have more effect). Specifically, as demonstrated in Table 5, module 1 with a smaller capacitance value difference among its SCs has a higher experimental and estimated final voltage value as compared to module 4 with a larger capacitance value difference. Therefore, in order to maximize power storage in an energy module, it is best to select SCs with the same capacitance or with a small difference so that, in the long term, more power can still be stored in the module. In this regard, one important motivation of the modelling work reported here is to gain understanding of the effects of the device-to-device variation in printed SCs on the performance of an energy module including several SCs connected in series.

Furthermore, the simulation results of the four ECMs can also be used as a method to predict the minimum and maximum voltage still remained in the energy module at any given time. In Table 5, the estimated final value of the voltage remained in each module (voltage at the end of day 31) based on different ECMs is given. According to this table, it is possible to determine the predicted minimum and maximum final voltage values for each module, and based on these values, one can approximate the possible final voltage range window over each module at the end of the 31st day. In support of this claim, as can be found in Table 5, the experimental result of voltage for each module at the end of day 31st is within the predicted final voltage range window.

4. Summary and conclusion

This study proposes a simplified equivalent circuit model (ECM) based on the experimentally identified parameters of supercapacitors (SCs) (EDLC type) in order to analyze their discharge and self-discharge characteristics. The proposed ECM utilizes experimental parameters of SCs such as capacitance value and ESR as well as an exponential function based on the experimental self-discharge profile of SCs to represent the nonlinear phenomena of self-discharge and leakage current. This article also proposes three very simple sub-ECMs by finding a linear relationship among the different parameters of the SCs used in developing the first ECM. Using these super-simple ECMs and merely knowing the capacitance and ESR value of the SCs, the discharge and self-discharge behavior of the EDLC-type SCs can be predicted over a long period of time with reasonable accuracy. In order to verify the accuracy of the proposed ECMs, simulation results for both the SCs used in the development of the ECMs and other SCs including two commercial EDLC-type SCs are compared with the experimental results and an excellent agreement is found. Moreover, a good match is observed between the simulation and experimental results of the discharge behavior of two SC energy modules, each consisting of three series connected SCs, connected to discrete resistive loads.

Literature-reported ECMs have more RC network elements and branches and are too complex to be used for multi-cell SC energy modules. Furthermore, those ECMs are not accurate in simulating the nonlinear self-discharge effect of SCs over a long period of time. In addition, some of the ECMs reported in the literature require a huge number of steps to define exponential functions and parameters to

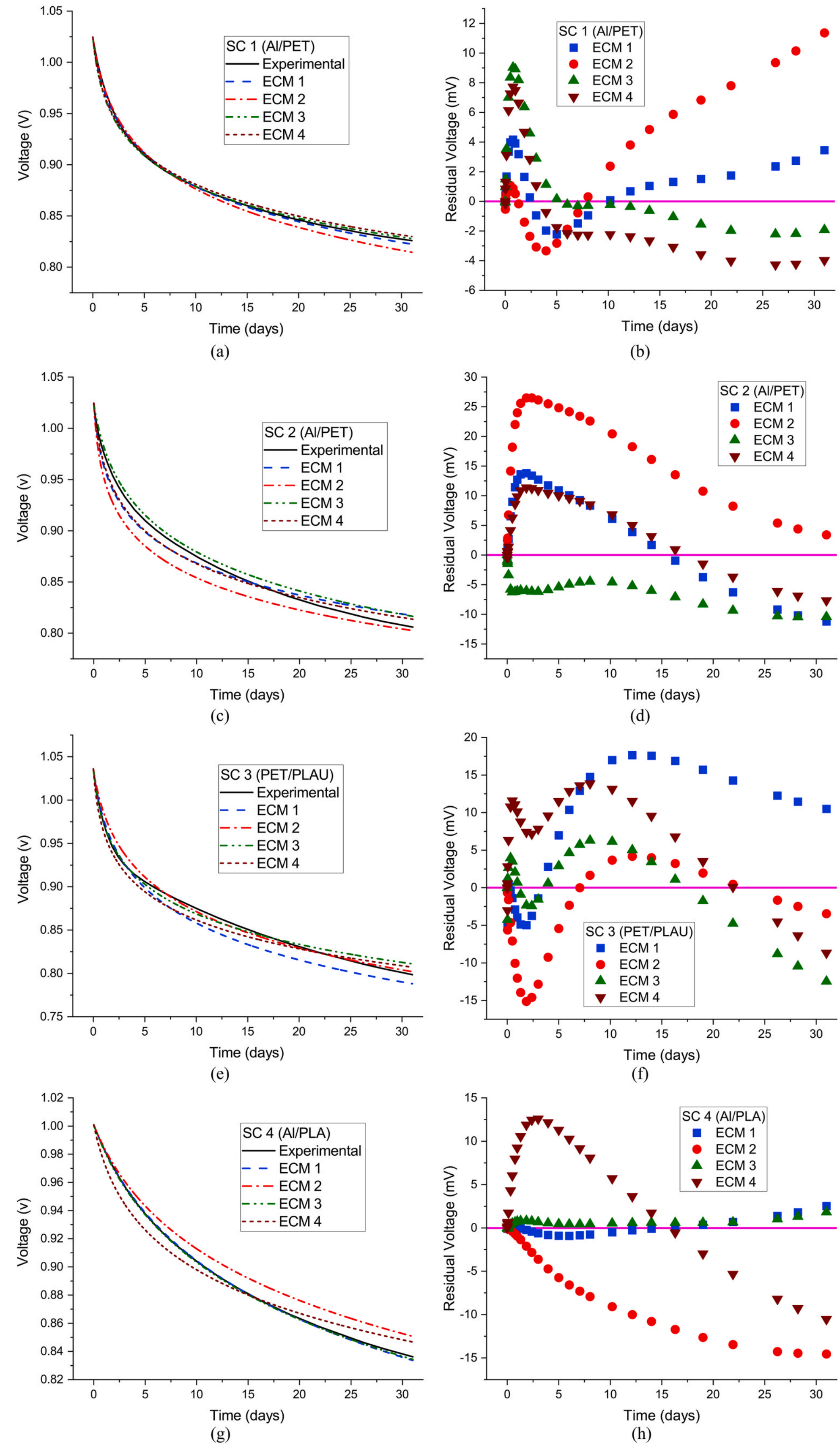


Fig. 6. a,c,e,g) Self-discharge experimental and simulation results in 31 days based on proposed ECMs for four randomly selected SCs not used to develop the ECMs. b,d,f,h) Residual voltage (the difference between experiments and simulations).

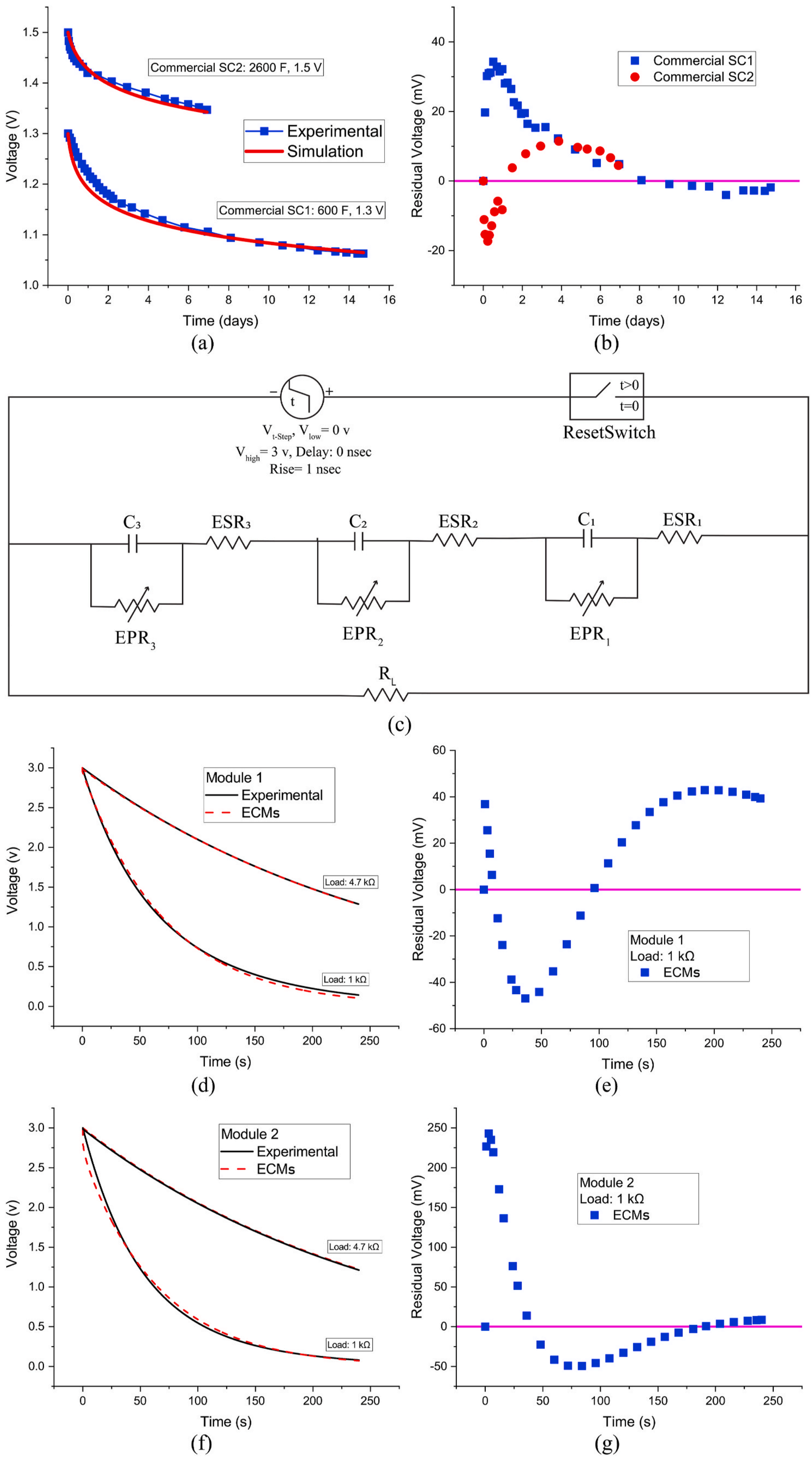


Fig. 7. a) Self-discharge experimental and simulation results based on ECM 4 of two commercially available SCs. b) Residual voltage (the difference between experiments and simulations) for the self-discharge of two commercial SCs. c) Charge and discharge ECM of a SC energy module (three series connected SCs) connected to a resistive load. d,f) Experimental and simulation results based on the proposed ECMs of the resistive load voltage during the discharge of the energy module. e,g) Residual voltage of the resistive load during the discharge of the module.

Table 4
ECM parameters of four SC energy modules, each consisting of three SCs connected in series.

Module 1	SC1	SC2	SC3	Module 2	SC1	SC2	SC3
C (mF)	147.7	158.8	161.3	**C (mF)**	140.5	183.4	222.2
ESR (Ω)	7.3	8	8	**ESR (Ω)**	7.2	7.8	8.8
a (EPR)	−34.7	−36.0	−36.8	**a (EPR)**	−34.0	−37.4	−39.0
b (EPR)	18.3	18.9	19.6	**b (EPR)**	17.1	21.4	23.8
C-total (mF)	51.9			**C-total (mF)**	58.6		
Module 3	SC1	SC2	SC3	**Module 4**	SC1	SC2	SC3
C (mF)	117.4	176.5	253.7	**C (mF)**	104.4	207.2	274.9
ESR (Ω)	7.5	7.4	8.4	**ESR (Ω)**	6.8	7	8.5
a (EPR)	−33.5	−36.2	−39.6	**a (EPR)**	−32.7	−38.3	−40.1
b (EPR)	16.3	20.2	24.8	**b (EPR)**	15.7	22.2	26.0
C-total (mF)	54.8			**C-total (mF)**	55.4		

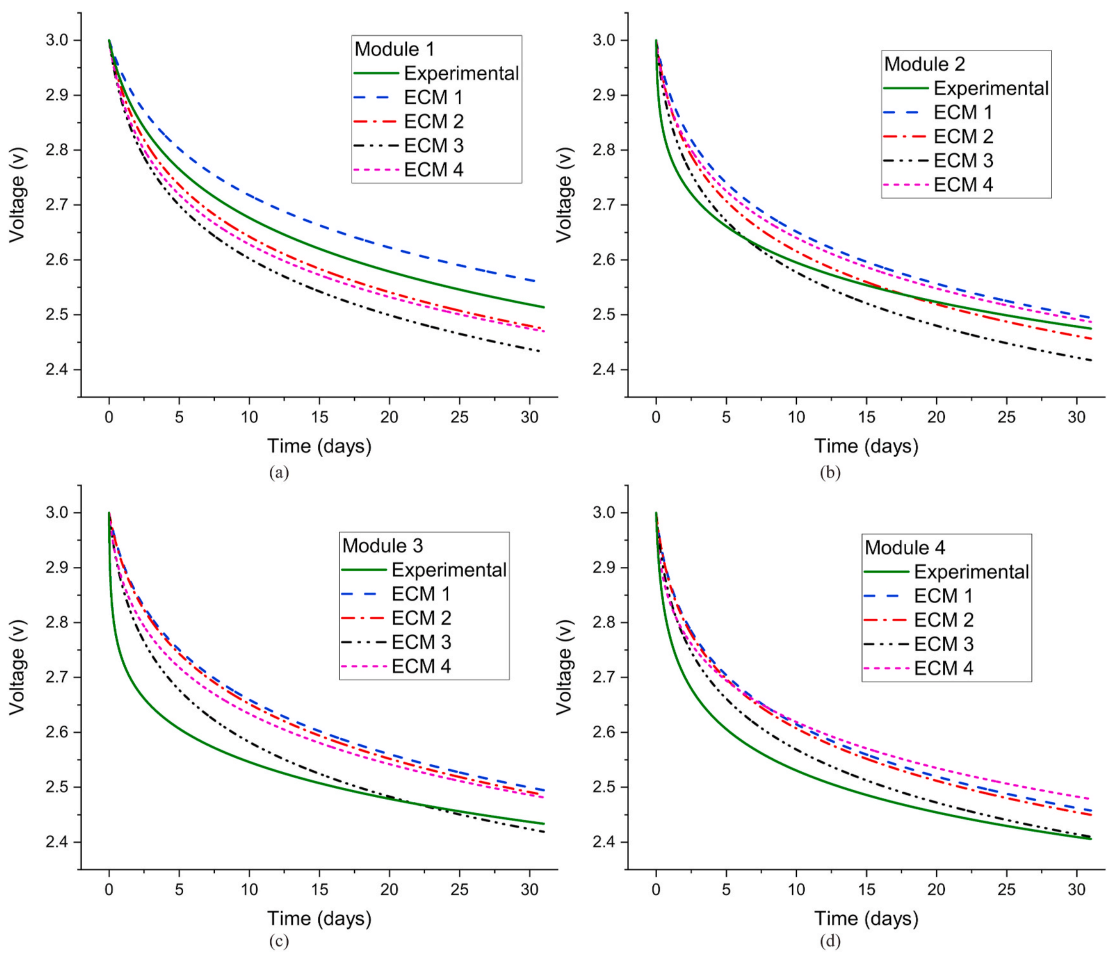


Fig. 8. Self-discharge behavior experimental and simulation results based on the proposed ECMs of four SC energy modules over time.

Table 5
Predicted final value of the voltage remained in each module (voltage at the end of day 31) based on proposed ECMs and experiments.

	Module 1	Module 2	Module 3	Module 4
ECM 1	2.56 V	2.49 V	2.49 V	2.46 V
ECM 2	2.47 V	2.46 V	2.49 V	2.45 V
ECM 3	2.43 V	2.42 V	2.42 V	2.41 V
ECM 4	2.47 V	2.49 V	2.48 V	2.48 V
Min.	2.43 V	2.42 V	2.42 V	2.41 V
Max.	2.56 V	2.49 V	2.49 V	2.48 V
Experiment	2.51 V	2.47 V	2.43 V	2.41 V

simulate the discharge behavior of SC modules over the long term. Due to the requirement for simple versions in order to implement the ECMs in practical applications, the ECMs presented in the literature are not suitable for long-term simulation of SC modules, despite their extensive RC network elements and difficulty in determining parameters. To conclude, the work presented in this paper, however, demonstrates a simple, practical, and accurate approach for studying the behavior of SC energy modules consisting of several SCs (EDLC type) connected in series/parallel, which can be used in the design of future energy storage systems and power management strategies. Furthermore, these ECMs may also be used to predict important aspects of printed electronics as well as the effect of different electrical variables that vary from device to device on the behavior of a SC energy module. Accordingly, depending on the applications, the proposed ECMs may affect the choice of materials and layer thicknesses to reduce the leakage current in SCs. A deeper investigation of these cases utilizing the Monte Carlo simulation tool will be the subject of the authors' upcoming research work in the near future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2023.232932.

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