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An improved exponential model for charge and discharge behavior of printed supercapacitor modules under varying load conditions

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HIGHLIGHTS

- Modelling charging and discharging of supercapacitors using an exponential method.
- The key parameters of supercapacitors are modeled based on experimental results.
- Proposed method models the nonlinear behavior of self-discharge and leakage current.
- Modelling supercapacitor modules over a wide range of load conditions in long-term.
- Fabrication steps of flexible printed supercapacitors are schematically summarized.

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ABSTRACT

We report an improved and simple exponential model for the charging and discharging behavior of series-connected modules of supercapacitors under varying load conditions and over extended periods of time. In this work, only a single variable leakage resistance (VLR) with exponential current/voltage profile is used to model the effects of different self-discharge mechanisms of a supercapacitor. Due to the simplicity and accuracy of the simulations, the proposed model can be implemented in practical applications, both short-term and long-term, unlike the two-, three-branch, and exponential models with voltage/time profile reported in the literature. We have modeled four different energy modules using the electrical parameters of 12 printed supercapacitors in order to study and compare the series connected supercapacitors' behavior in each energy module. The key parameters such as capacitance and equivalent series resistance (ESR) of supercapacitors were based on experimental results. The numerical exponential method reported here enables modelling of the nonlinear behavior of self-discharge and leakage current over a wide range of load conditions and time periods. Furthermore, we have modified the linear model reported in the literature for leakage and self-discharge and compared the results with our nonlinear model.

1. Introduction

Energy storage systems [1] play a key role in storing the harvested energy generated from renewable readily available sources like wind [2], light [3], bio-energy [4], and RF radiation [5], as well as delivering the needed energy to the system when high power is required or when the primary energy source is not available [6–8]. Energy-Harvesting Wireless Sensor Nodes [9–12], energy autonomous Internet of Things (IoT) [13–16] and trillions of sensor networks in the near future will connect smart devices for different applications such as healthcare [17], security [18], smart home automation systems [19] and wearable electronics [20]. Hence, energy storage systems are a subject of continually growing research interest, as these systems will play a key role in a variety of future applications. Furthermore, with the increasing attention to directly integrate energy harvesting and storage devices to achieve flexible, stretchable, and wearable self-charging sensors and power systems [21–28], the importance of inexpensive and environmentally friendly energy storage systems is increasing day by day [29, 30]. The task of these systems is to store the energy supplied by other sources and to provide the instantaneous electrical power required by the system [31]. The main criteria for an energy storage system include high specific power and energy density, fast charging time, reliability,

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low power dissipation and longevity [32].

Supercapacitors (SCs) [33,34], sometimes referred to as electric double layer capacitors (EDLCs), have been modeled and analyzed like regular capacitors, despite being larger in capacity. Over the past decade, extensive studies and research have been conducted on SCs as a key element in energy storage systems [23–28,35,36]. SCs are promising elements for use in energy harvesting and storage systems, due to their large specific power density, high efficiency, fast charge and discharge time, low heating losses because of small equivalent series resistance (ESR), and long lifespan (in both charge/discharge cycles and time) and are widely used in energy storage systems and hybrid energy systems with batteries [37–40]. In addition, SCs are, in many cases, a good alternative to batteries due to disposability, safety, and long lifetime [41,42]. The voltage range for a single SC is low, as it is limited to the electrochemical window of the electrolyte. For applications that require high voltage, multiple SCs can be connected in series to form a SC energy module that can be integrated directly to the energy storage systems.

Modelling SC energy modules is essential from the viewpoint of design prediction and condition monitoring [43]. Modelling the various electrical properties of SCs and predicting the effect of these properties on charging and discharging behavior of an energy module, both in the presence or absence of a load, are important steps before utilizing SCs in energy modules. In particular, due to the potential device-to-device variation in electrical properties, especially in printed SCs, it is important to model and understand the effect of these variations on the performance of series-connected modules.

There are numerous models reported in the literature for SCs with the aim of accurately describing their electrical behavior [43–45], thermal behavior [43–45], self-discharge [43–46], and aging [45] under different operating conditions. In order to model the electrical behavior of SCs, one of the most common modelling methods is the equivalent circuit model, which uses parametric RC (resistor-capacitor) networks. Although the equivalent circuit model does not explicitly state the physical parameters and internal information of SCs, this model is derived from experimental data and empirical experience. Furthermore, the simple structure and high accuracy of this model make it suitable for real-time energy management applications [48]. In the parametric RC networks model, depending on the configuration of the electrical circuit and the number of elements, the accuracy of the circuit model varies. The basic equivalent circuit model, known in the literature as the classical equivalent circuit, is a subset of parametric RC networks; it includes a capacitor C and an equivalent series resistance (ESR) to model the internal losses of the SC [49]. The advantage of this classic RC model is its inherent simplicity. On the other hand, in this model, the effects of self-discharge and leakage of SCs in the system cannot be observed and analyzed. Spyker et al. [50] added another constant resistance parallel to the capacitor in the classical model, with the aim of considering the phenomenon of self-discharge and leakage current (Fig. 1a). However, self-discharge and leakage current of SCs is a nonlinear phenomenon and cannot be modeled with a constant parallel resistance. On the other hand, the effects of self-discharge and leakage of SCs during long-term charge/discharge time are significant, and therefore the classical RC model and Spyker model can only be useful in very short-term (several seconds) charge/discharge time; this significantly limits the range of realistic applications of these models.

Moreover, there are somewhat more complicated equivalent circuit models with more RC network elements for SCs reported in the literature, such as a two-branch model with equivalent parallel resistance (EPR) [51] and a three-branch model [52]. In the two-branch model with EPR (Fig. 1b), the first branch is the main branch, where R_0 and the voltage dependent capacitance (C_0 and $K_V \cdot V$) are connected in series. This branch represents the charge and discharge behavior of the SC in the short-term. The second branch, which has R_2 and C_2 in series, determines the redistribution of the SC charge in the mid-term and long-term, and the constant equivalent parallel resistance (EPR) models the self-discharge effect. Since this model uses a constant parallel resistance, it considers only the internal ohmic leakage of the SC and is not a suitable model for estimating the SC non-linear self-discharge effect in the long-term. In the three-branch model (Fig. 1c), another branch, with R_r and C_r in series, is added to define the self-discharge caused by diffusion-controlled Faradaic redox reactions, which is proportional to the concentration gradient of the diffusible redox species. The concentration gradient, at a certain distance from the electrode, is inversely proportional to the square-root of time and, consequently, leads to a decrease in the rate of self-discharge over time. Nevertheless, despite the complexity of the model and a greater number of RC network elements, this model is also not able to well estimate the nonlinear effect of self-discharge in SCs in the mid-term to long-term.

In other work, a variable leakage resistance (VLR) is used to model the self-discharge time dependency in a SC [53,54]. In this model (Fig. 1d), several distinct exponential functions are used to model the self-discharge characteristic, each of which has different time constants at different time and voltage periods of self-discharge, leading to varying leakage resistances. Zhang et al. [53,54] reported to have found by trial and error that modelling the self-discharge effect of a SC for 8 h required five distinct exponential functions for five periods. In another VLR model published by Ghanbari et al. [55], multiple distinct exponential functions with voltage/time profiles have been used to model the effect

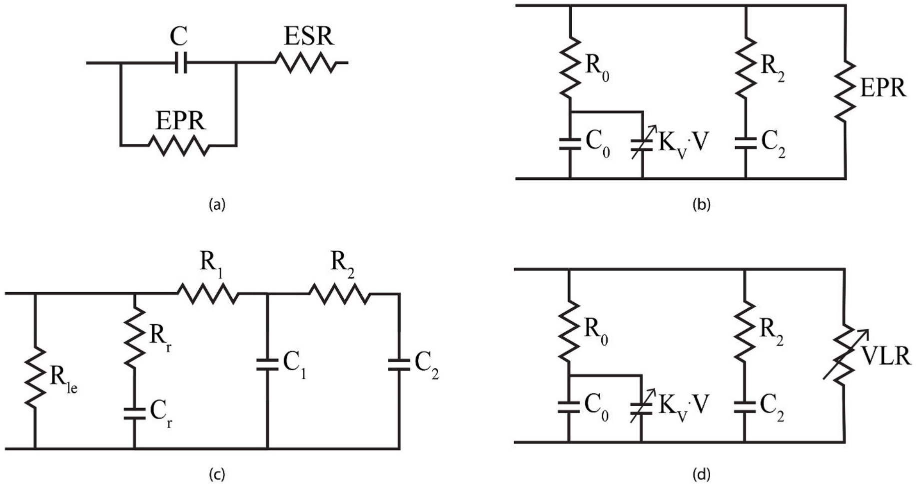


Fig. 1. Equivalent circuit models reported in the literature for a single SC; a) Spyker et al. model [50]. b) two branch model with EPR [51]. c) three-branch model [52] and d) VLR model [53–55].

of supercapacitor self-discharge in the short term (6 h). It is clear that, in order to analyze and study the behavior of series connected SC modules self-discharge using these VLR models [53–55] in the long term (one month for example), a very large number of distinct exponential function characteristics are required for different periods, which requires many parameters determination steps. For this reason, using these VLR proposed models [53–55] would increase the difficulty of parameter identification in SC energy modules, thus practically the reported VLR models are not suitable for long-term simulations.

In this work, we have in brief illustrated the fabrication steps and characterization of our disposable and flexible printed SCs using low-cost and non-toxic processes and materials. In the following, we have presented a numerical exponential method to model the nonlinear behavior of self-discharge and leakage current of SCs using experimental electrical parameters of SCs. We report an improved model based on experimentally determined quantities of individual devices. The model also predicts the dependence of the operation of series-connected modules on variation of electrical properties from device to device, an important issue in printed devices. In other words, in addition to its ability to model the full charging and discharging behavior of the supercapacitors, the model can also be used to study the effect of device-to-device variations in electrical parameters, especially the nonlinear nature of leakage current and self-discharge, on the behavior of series connected supercapacitors in the energy modules. In contrast to the models [53–55] using a variable leakage resistance with exponential voltage/time profile, the model proposed in this work uses variable leakage resistance with exponential current/voltage profile. In addition, the method of obtaining the exponential profiles is different; in our model, it is based on experimental data of SCs self-discharge for a long time (31 days). Furthermore, in the model presented in this paper, no distinction is made between different self-discharge mechanisms. Rather, a single VLR with exponential current/voltage profile has been introduced to consider the effects of various self-discharge mechanisms under the normal operation conditions.

Briefly, the two-branch model with EPR, three-branch model and VLR models reported in the literature, have multiple branches and more RC network elements, while in practical applications, simplified versions are required to enable model implementation. In contrast, the proposed model has only one branch and a few RC elements (only 3), and accordingly is simpler for use in energy storage modules which include several SCs in series.

Furthermore, as an illustration, we have also modeled four different energy modules using the parameters of 12 printed SCs in order to simulate the SCs' behavior in energy modules. We have simulated the charging and self-discharging behavior of the modules to estimate their behavior in the absence of load and the amount of power delivered to different small and large loads in short-term and long-term. We have also modified the Spyker model reported in the literature [50] and compared the simulation results of the model proposed in this work with the modified Spyker model.

2. Experimental and methods

2.1. Fabrication of supercapacitors

The fabrication process for this type of printed supercapacitors (SCs) has been reported in the previous works published by the group [39,40,56–61] but will be summarized here. The fabrication steps are shown schematically in Fig. 2. A double-sided Al/PET flexible substrate (Pyroll) was used as the starting substrate with an aluminum (Al) thickness of 9 μm and a polyethylene terephthalate (PET) thickness of 50 μm (Fig. 2a). Before fabrication, the Al/PET substrate was pre-heated inside the oven at 95° for 15 min (Fig. 2b).

First, a current collector layer consisting of a graphite ink (Acheson Electrodag PF-407C) was applied onto the PET side of the substrate, while the Al layer acts only as a barrier layer (Fig. 2c). The graphite ink was then dried in the oven for 1 h at 95° (Fig. 2d) and a graphite thickness of 40–50 μm was obtained. Subsequently, activated carbon was applied using an in-house formulation with chitosan as binder to form an electrode layer onto the current collector layer (Fig. 2e). The activated carbon ink was then dried at room temperature overnight (Fig. 2f) and the resulting film was 50–70 μm thick. A laboratory scale doctor blade coater was used to deposit these layers. Then, heat-sealing dispersion adhesive material (Paramelt Aquaseal X2277 polyolefin) was applied onto the PET and part of the current collector layer (Fig. 2g). The samples were then placed in the oven at 80 °C for 15 min (Fig. 2h). NaCl: H_2O aqueous electrolyte with a mass ratio of 1: 5 was then added onto the electrode layer (Fig. 2i). The next step was to add a paper separator onto the electrode, in which the electrode and the paper separator were impregnated with aqueous electrolyte (Fig. 2j). Fig. 2k shows the other half of the SC, which is shown upside down in the figure. The electrode in Fig. 2k was exactly the same pattern as the electrode in Fig. 2j, but facing downwards, and without the paper separator. In the final step, the two electrodes were packed and heat-sealed face to face with the help of annealed Aquaseal, as shown in Fig. 2l, upside down. The final length, width, and thickness of the fabricated SC with the package were 50, 50 and 0.4–0.5 mm, respectively.

2.2. Characterization of supercapacitors

The key electrical parameters of SCs, such as capacitance, equivalent series resistance (ESR) and leakage current were obtained using an international industrial standard, IEC 62391-1 [62]. A Maccor 4300 workstation (Maccor Inc., USA) was used to electrically characterize the SCs. The SCs were charged and discharged three times between 0 and 1.2 v with a constant current of 1, 3 and 10 mA. The SCs were then held at the constant voltage of 1.2 V for 30 min. The capacitance was measured through a constant current discharge step between 0.96 V and 0.48 V. The SCs were then kept at the constant voltage of 1.2 V for 1 h and the leakage current was obtained. This was repeated for all three currents of 1, 3 and 10 mA. Eventually, the ESR was calculated from the IR drop in the measurement with discharge current of 10 mA.

2.3. Improved equivalent circuit model

As mentioned in the introduction, equivalent circuit models reported in the literature are inefficient for long-term applications due to the lack of thorough treatment of leakage and self-discharge effects [43–55]. In order to overcome this limitation, the nonlinearity of leakage and self-discharge is modeled in this work. To do this, each of the fabricated supercapacitors (SCs) was first charged to about 1 V, and then during self-discharge, their voltage and current were recorded for 31 days, and their current-voltage exponential equation was extracted from the experimental data. As shown in Fig. 3b, the exponential equation for the current-voltage curve of one of the SCs is extracted with a good approximation. This was repeated for all 12 printed SCs used in this work, and a unique exponential and nonlinear equation for the leakage of each SCs was obtained.

In order to model the internal parameters of a SC (Fig. 3a), each device is modeled with a capacitor, a series resistor called ESR, as well as a variable exponential element connected in parallel with the SC to model the nonlinearity of SC self-discharge and leakage current. The values of capacitance and ESR from the characterization of the printed SCs using the Maccor system and the values of 'a' and 'b' from the experimental data of SCs during self-discharge are given in the model. 12 SCs were fabricated and characterized, each of which had its own unique capacitance, ESR, 'a' and 'b' values.

This exponential model for SC self-discharge and leakage, while maintaining the simplicity of the circuit structure, also increases the accuracy of the simulation and is suitable for long-term simulations, compared to the linear models reported in the literature [43–55]. To show this, the self-discharge behavior of a SC is simulated using the

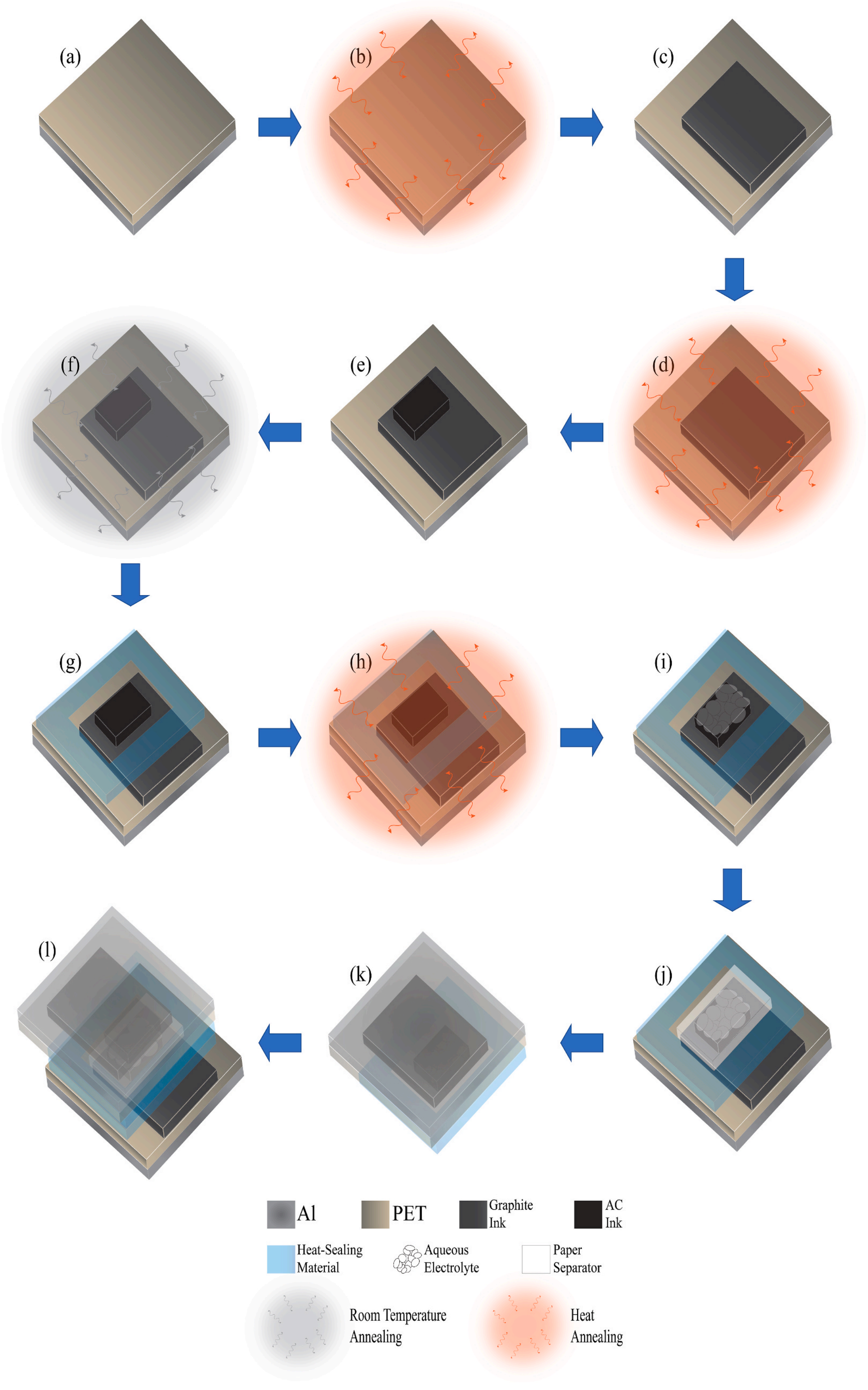
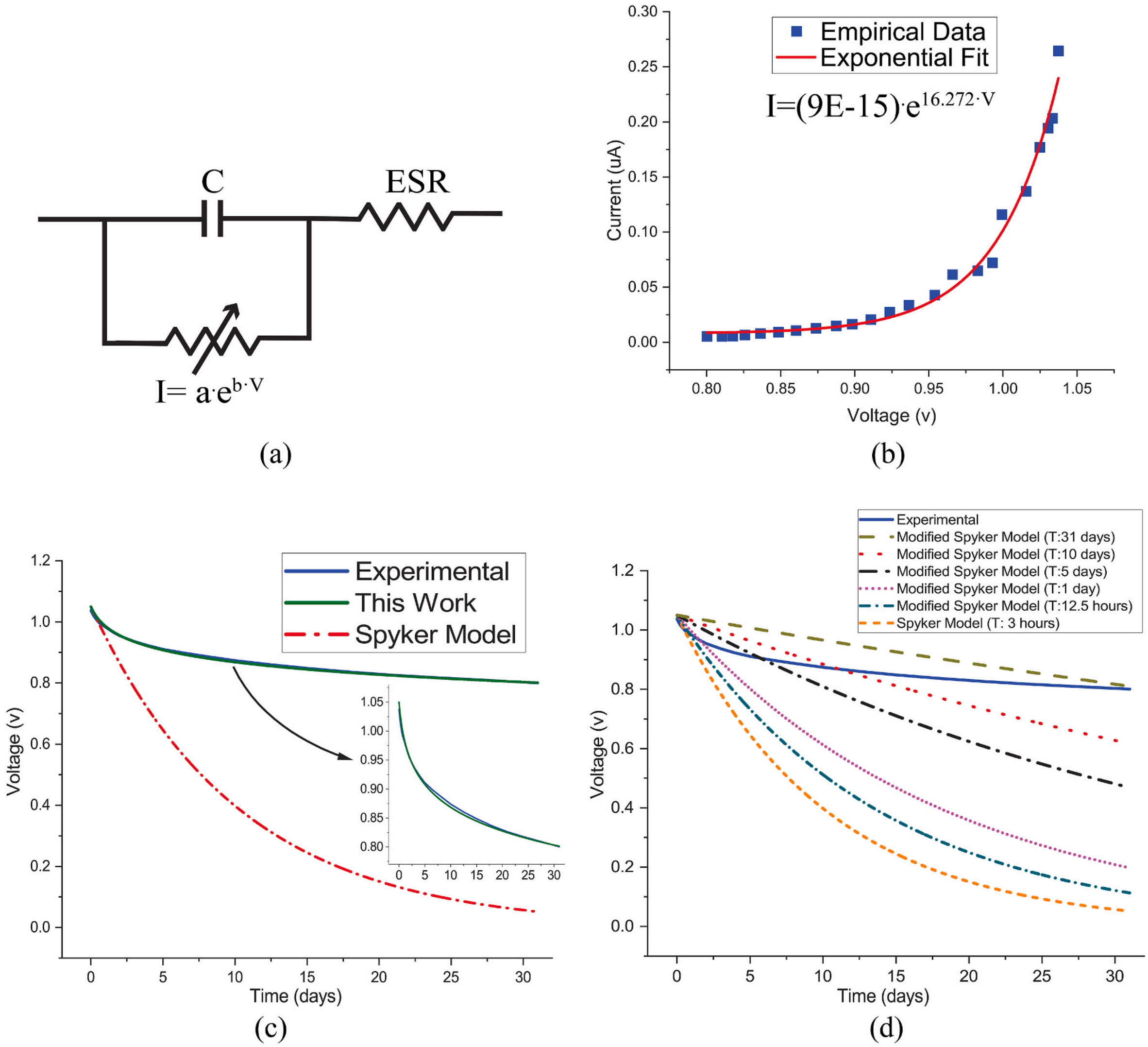


Fig. 2. Complete fabrication steps. a) The starting substrate; A double-sided Al/PET flexible substrate, 9 μm Al, 50 μm PET. b) Pre-heating the substrate in the oven at 95° for 15 min. c) Developing the current collector layer using graphite ink. d) Drying graphite ink in the oven for 1 h at 95°. e) Developing the electrode layer using activated carbon ink with chitosan binder. f) Drying activated carbon ink at room temperature overnight. g) Applying heat-sealing adhesive layer onto the PET and part of the current collector layer. h) Annealing the heat-sealing layer in the oven at 80 °C for 15 min. i) Adding NaCl: H2O aqueous electrolyte with a mass ratio of 1: 5 respectively. j) Adding the paper separator. k) Second cell upside-down without the separator. l) Heat-sealing and packing two cells together face to face upside-down using annealed heat-sealing adhesive layer.



(a) (b)

(c) (d)

Fig. 3. a) Proposed equivalent circuit model of a SC. b) Extraction of I–V exponential equation for leakage current and self-discharge modelling. c) Self-discharge behavior of a SC modeled by Spyker linear model and the exponential model proposed in this work and comparing the results with the experimental results. d) The modified Spyker model; albeit closer to the experimental results by applying longer self-discharge time constant (T) to the proposed equation, but still does not fully comply with the experimental results.

linear model reported by Spyker et al. [50] and the exponential model presented in this work, and the results are compared with the experimental data. Using the method provided by Spyker et al. [50], the constant equivalent parallel resistance (EPR) for modelling the self-discharge and leakage was calculated and included in the equivalent circuit model in parallel with the capacitor (Fig. 1a) and the SC self-discharge was simulated. As can be seen in Fig. 3c, it is clear that the Spyker linear model is not suitable for simulating the discharge behavior of a SC in long-term applications, and in contrast, the model presented in this work is very accurate and the results obtained from the simulation are in good agreement with the experimental results. However, the equation in the Spyker method for calculating the EPR considers the values of self-discharge voltage only for a period of 3 h. We modified this method and calculated the EPR values by applying the self-discharge values for longer time constants, as can be seen in Table 1. Fig. 3d shows that by applying the self-discharge values to the Spyker equation over longer time constants, the SC self-discharge behavior approaches the experimental results, but is still far from fully consistent with it.

Table 1
The calculated EPR values for longer time constants using Spyker method reported in literature [50].

Time Constant	EPR (M Ω)
3 h	4.9
12.5 h	6.6
1 day	8.8
5 days	18.1
10 days	27.5
31 days	56.4

In this work, we have modeled 4 different SC energy modules using 12 SCs, each of modules consists of 3 series connected SCs. To model the SCs, the exponential model described earlier in Fig. 3 was used. Using this model, the charging and discharging behavior of SCs in the form of energy modules, the total amount of power delivered to different loads by 4 modeled energy modules, and the self-discharging behavior of the modules are discussed and analyzed. Fig. 4a shows the equivalent circuit model of an energy module while charging. This equivalent circuit, in addition to three SCs in series, has a step-source battery to charge the SCs and a resistor parallel to the whole circuit to model the load connected to the energy module. Fig. 4b shows the equivalent circuit of an energy module during discharge. A DC voltage source is modeled in parallel with each SC, and the voltage value of this source is the final

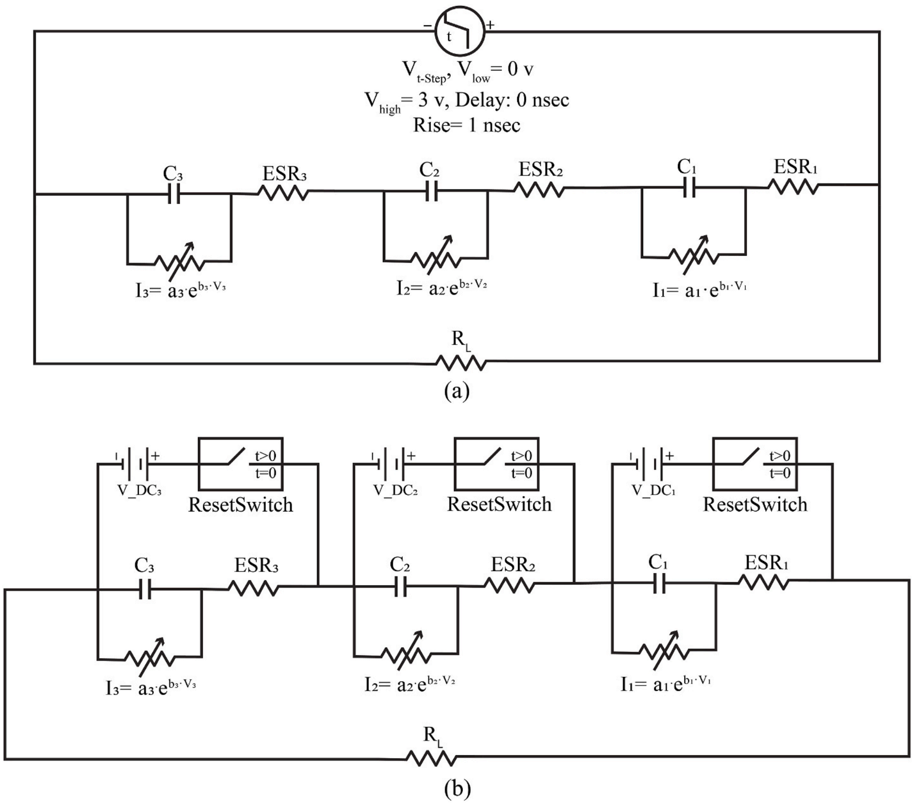


Fig. 4. a) Charging circuit model of a SC energy module. b) Discharging circuit model of a SC energy module.

value of the potential difference stored in the SCs at the end of the charging phase. In order to show that this potential difference is stored at the two ends of the SCs at zero seconds, a reset switch is modeled in series with each source. In this work, we have modeled 4 different scenarios using 12 different SCs. The capacitance, ESR, and exponential equation parameters related to self-discharge of each SCs which used in 4 different energy modules are shown in Table 2. The capacitance of these SCs is between 146 and 222 mF, the equivalent capacitance of each module is about 60 mF and the ESR value of the SCs is between 6.3 and 9.9 Ω.

3. Results and discussion

3.1. Accuracy of the proposed model

In order to verify the performance of the model presented in this work, the test of connecting discrete resistors to SC modules was performed. In this experiment, SC modules 1 and 3 were randomly selected and three different discrete resistors were used as the resistive load. The voltage value of the two ends of the resistor during discharge of the SC modules was measured using a digital multimeter. The resistance values of the resistors used were 1.0, 4.7 and 8.2 kΩ and the measured experimental results were compared with the simulation results. As can be seen in Fig. 5, the difference between the simulation and experimental results is negligible. Therefore, it can be concluded that the proposed model is well verified against experiments.

3.2. Effect of leakage current during charging

In order to understand the leakage current effect of the supercapacitors (SCs) on the potential difference stored at their ends, simulations were performed with and without consideration of the leakage. In Fig. 6a and Fig. 6b, the voltage stored in the SC_1 over time in module 1 during charging is shown. As can be seen, the leakage current has very little effect on the stored voltage. This simulation was repeated for all SCs in all four energy modules, and all the results showed that there was truly a slight difference between the two diagrams. Therefore, it can be said that leakage current has negligible effect on the charging behavior of SCs in the energy modules, and leakage current can be ignored during charging as long as the leakage current is considerably smaller than the charging current.

Furthermore, as can be seen in Fig. 6c and d, the final amount of the

Table 2

Parameters of SCs used in four energy modules; each energy module contains three series connected SCs.

Module 1	SC_1	SC_2	SC_3	Module 2	SC_4	SC_5	SC_6
Capacitance (mF)	181.7	183	176.8	Capacitance (mF)	188.3	158.4	172.6
ESR (Ω)	8.4	7.8	7	ESR (Ω)	7.2	9	7.4
EPR Factors	$a_1 = 7E\text{-}15$ $b_1 = 16.225$	$a_2 = 9E\text{-}15$ $b_2 = 16.272$	$a_3 = 3E\text{-}14$ $b_3 = 15.217$	EPR Factors	$a_4 = 1E\text{-}14$ $b_4 = 15.638$	$a_5 = 1E\text{-}15$ $b_5 = 16.991$	$a_6 = 5E\text{-}14$ $b_6 = 14.675$
Module 3	SC_7	SC_8	SC_9	**Module 4**	SC_{10}	SC_{11}	SC_{12}
Capacitance (mF)	147.8	178.8	209.3	Capacitance (mF)	145.9	184.8	222.2
ESR (Ω)	9	8.1	7.1	ESR (Ω)	7.3	6.3	9.9
EPR Factors	$a_7 = 7E\text{-}15$ $b_7 = 15.508$	$a_8 = 1E\text{-}15$ $b_8 = 10.903$	$a_9 = 6E\text{-}14$ $b_9 = 13.444$	EPR Factors	$a_{10} = 9E\text{-}14$ $b_{10} = 8.4903$	$a_{11} = 4E\text{-}15$ $b_{11} = 17.591$	$a_{12} = 3E\text{-}15$ $b_{12} = 17.054$

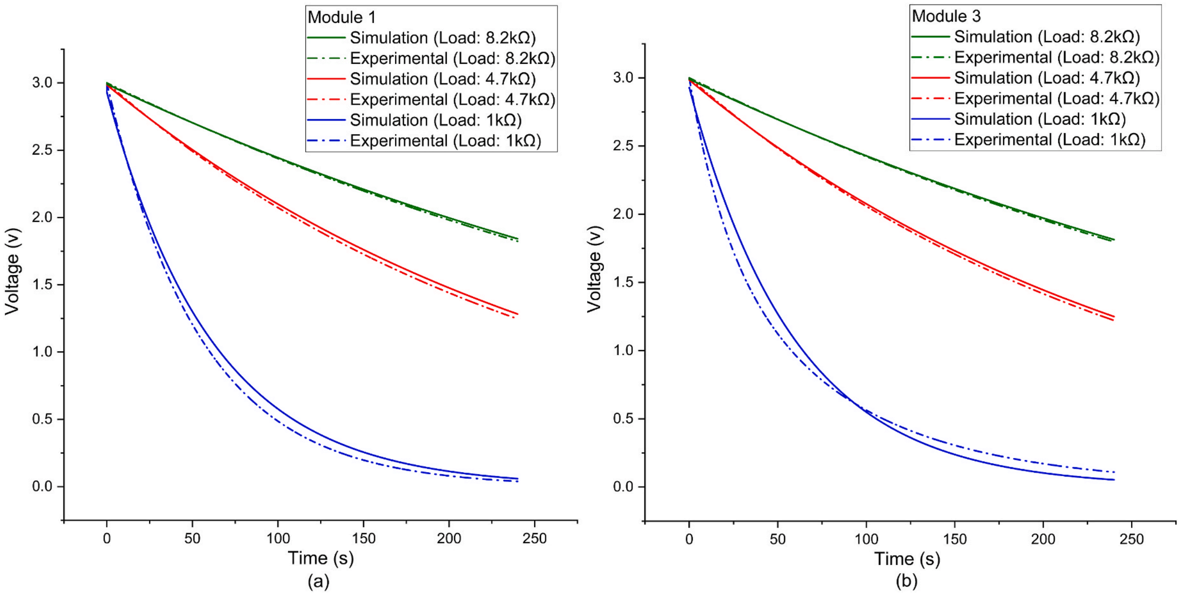


Fig. 5. Verification of the proposed model accuracy against experiments using carbon resistors as resistive loads. Experimental and simulation behavior of a) SCs module 1, b) SCs module 3.

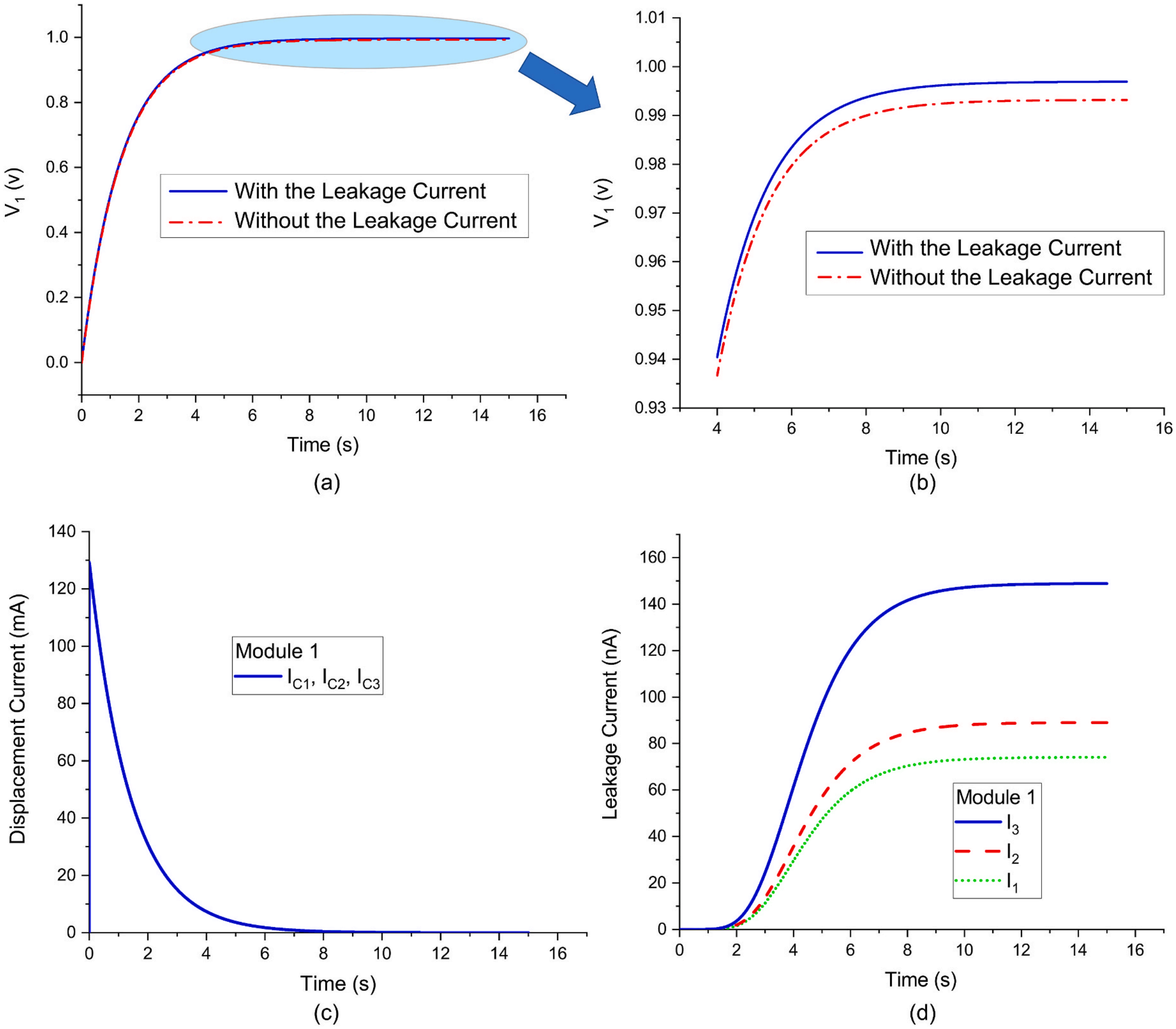


Fig. 6. a), b) Investigation of the leakage current effect on the charge of SCs in energy module 1. c), d) Comparison of the displacement and leakage current of the SCs during charging in energy module 1.

leakage currents is around 10^6 times smaller than the initial amount of the displacement currents. This simulation was also performed for the other three energy modules and similar results were observed for all modules. These results confirm that leakage current has little effect on the charging behavior of the SCs in energy modules and can be ignored.

3.3. Discharging behavior

In order to simulate the discharge behavior of SCs in energy modules, a resistor parallel to the system was used to model the load connected to the energy modules (Fig. 4b). Since these printed SCs can be used in a variety of applications such as Internet of Things (IoT), flexible and wearable electronics, energy harvesting wireless sensor networks, etc., and in both short-term and long-term applications, both large loads in the MΩ range and small loads in the kΩ range were simulated. The self-discharge, as well as the voltage delivered by module 3 to the different large load resistance values using the modified Spyker model (time constant: 31 days) and the model presented in this work, can be seen in Fig. 7a. The results for the simulation using the Spyker model are shown with a dash-dotted line and the results for the simulation using the model presented in this work are shown with a straight line. As can be seen in Fig. 7. a, upon increasing the resistive load in the long-term, especially during self-discharge, the Spyker model does not provide an accurate estimate of the behavior of the energy module. In addition, the modified Spyker model is no longer able to accurately estimate the final amount of the voltage stored in the SC energy module. On the other hand, as the accuracy of the model presented in this work with the empirical results was confirmed earlier in this article, it can be said that, for example, when self-discharging, there is still more than 2.5 V potential differences stored in this module after 30 days. While the 100 MΩ load is connected, the module, after 20 days of delivering power, is still able to deliver more than 2 V to the load. For other modules, similar results were obtained. In Fig. 7b, the amount of voltage delivered to the relatively small loads (range in kΩ) by module 3 using the model proposed in this work is shown over time. For example, when a 5 kΩ resistance load is connected to the module 3, after 2 min, there is still about 2 V stored in the energy module containing three series connected SCs.

We now compare the performance of the different modules when connected to the same resistive load during discharge as well as the self-discharge using the modified Spyker model, and the model proposed in this work. Fig. 7c shows the voltage delivered from the four modules to the same resistive load (100 MΩ) over time. As can be seen, module 4 shows better performance than the other modules. Module 3 delivers less voltage initially than modules 1 and 2, but performs better later on, and delivers higher voltage after the 6th day. The simulations were repeated for additional resistive loads in the range of MΩ, and in all simulations, module 4 had better performance in delivering more power to the loads over time. Fig. 7d shows the self-discharge of the four energy modules over time using the modified Spyker model and the proposed model; Straight lines show the results of the simulation using the proposed model and dash-dot lines also show the results of the modified Spyker model. Module 4 has again a relatively better performance than the other three modules using both models. However, the simulation using the modified Spyker model cannot even accurately estimate the final values of the potential difference stored in the modules while self-discharge and differs significantly from the simulation results using the proposed model.

The same comparison for delivering voltage from the energy modules was carried out for smaller resistance loads (in the range of kΩ) over shorter time (120 s). In Fig. 7e and f, the voltage delivered by different modules to a 5 kΩ resistive load using the model proposed in this work and the Spyker model can be seen, respectively. For this load, all four modules have almost the same performance using both models. The same simulations were performed for several other resistive loads in the kΩ range, from 1 to 500 kΩ; similar results were obtained for both models and there was no significant difference between the modules' performance. This is due to the fact that the simulations for small resistive loads were performed for a short time (120 s), and as already mentioned in the Introduction, leakage current has little effect on the discharge behavior of SCs in the short-term. Therefore, all four energy modules show almost identical self-discharge and leakage behavior. As a result, the modules have the same performance in delivering power to the small resistive loads.

The reason for the better performance of Module 4 in delivering more power to the loads in long-term is related to the leakage behavior of the SCs in this module. By comparing the leakage currents of the 12 SCs in the four energy modules, it can be seen that the three SCs in module 4 have smaller leakage current than the SCs in the other modules. Fig. 8a, 8b, 8c, 8d shows the leakage current of the SCs in each of the four energy modules and it is clear that the three SCs that form module 4 have a lower total leakage current than the other SCs, and therefore module 4 has a better performance in delivery of more power to the different loads in the long-term. Therefore, based on the simulation results of the proposed model, it can be said that device-to-device variations in electrical properties, especially leakage current in printed SCs, which are typically encountered in printed devices can affect the performance of series-connected SC modules, but not to the extent that their usability or stability is significantly reduced. In addition, the leakage behavior of the SCs that form each module using the modified Spyker model can be seen in Fig. 8a, 8b, 8c, 8d. As can be seen in this figure, using the modified Spyker model, linear curves are obtained for the leakage currents, which does not correspond to the nonlinear leakage behavior of SCs in reality.

3.4. Effect of resistive load on the leakage current of supercapacitors

According to the discharge model of the SC modules (Fig. 4b), as the resistance load increases, the significance of the leakage current of the SCs in the energy modules increases. For example, Fig. 8e and 8f shows the leakage current of the SC1 in the energy module 1 for the different small and large resistive loads. As can be seen in this figure, the highest leakage current is for the self-discharge and the lowest is when a 1 kΩ resistive load is connected to the energy module. This happens because as the resistive load increases, less voltage is delivered from the SCs to the load, hence more potential difference remains in the SCs and since the leakage current has an exponential relationship with the potential difference over the SC, the leakage current remains higher due to the larger potential difference between the two ends of the SC.

4. Summary and conclusion

In this paper, we present a simple equivalent circuit model for supercapacitors (SCs) energy module based on exploiting the experimental parameters of printed SCs. The model includes both the equivalent series resistance (ESR) and an exponential equation to account for the non-linearity of leakage current and self-discharge. These experimental parameters, which are unique for each SC, contribute to the effective simulation and design of future systems. In addition, this model can be used to predict important issues in the printing of devices, as well as the dependence of an energy module consisting of series connected SCs on different device to device electrical variables.

The proposed model was used to investigate the effect of leakage current while charging SCs in four energy modules. In addition, the results of the self-discharge of each module and the amount of energy delivered to the different loads by four energy modules were compared with the model reported in the literature [50]. Finally, the effect of changing the resistive load on the time-dependent leakage current of SCs in an energy module was investigated. Furthermore, an analysis of the effect of device-to-device variations on the performance of the modules showed that typical variations in printed devices are not sufficient to cause significant problems in operation.

As SCs have been widely discussed in the literature as a promising

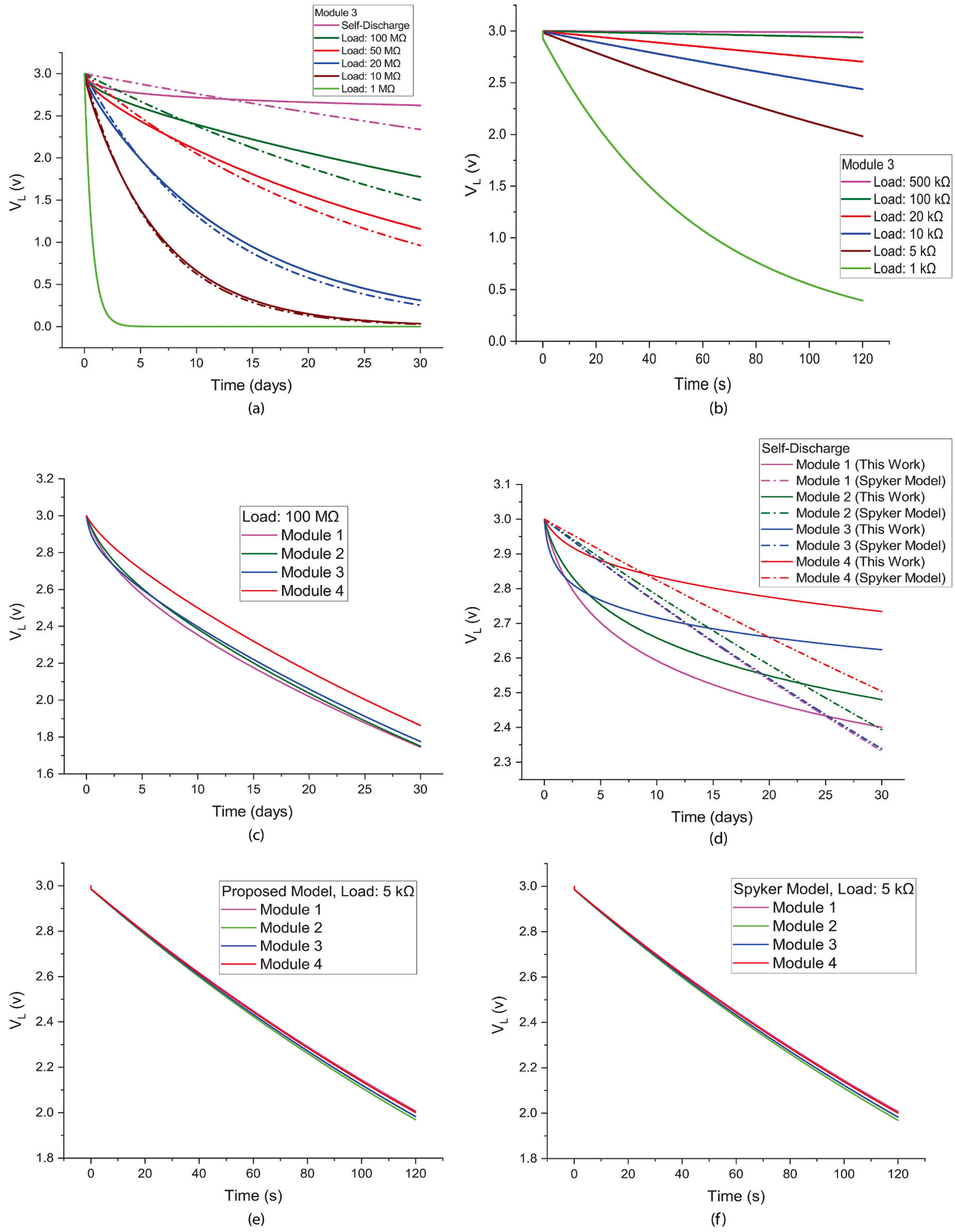


Fig. 7. a) Self-discharge behavior and the voltage delivered to the different large loads by the energy module 3 over time using the modified Spyker model and the model proposed in this work; The modified spyker and the proposed model are shown with dash-dotted and straight lines, respectively. (b) Voltage delivered to the different small loads by the energy module 3 over time using the model proposed in this work. (c) Comparing the voltage delivered to a 100 MΩ resistive load by four different energy modules. (d) Self-discharge behavior of four energy modules using the Spyker model and the proposed model; The modified spyker and the proposed model are shown with dash-dotted and straight lines, respectively. e) Comparison of the voltage delivered to a 5 kΩ resistive load by four different energy modules in short-term using the proposed model. f) Comparison of the voltage delivered to a 5 kΩ resistive load by four different energy modules in short-term using the Spyker model.

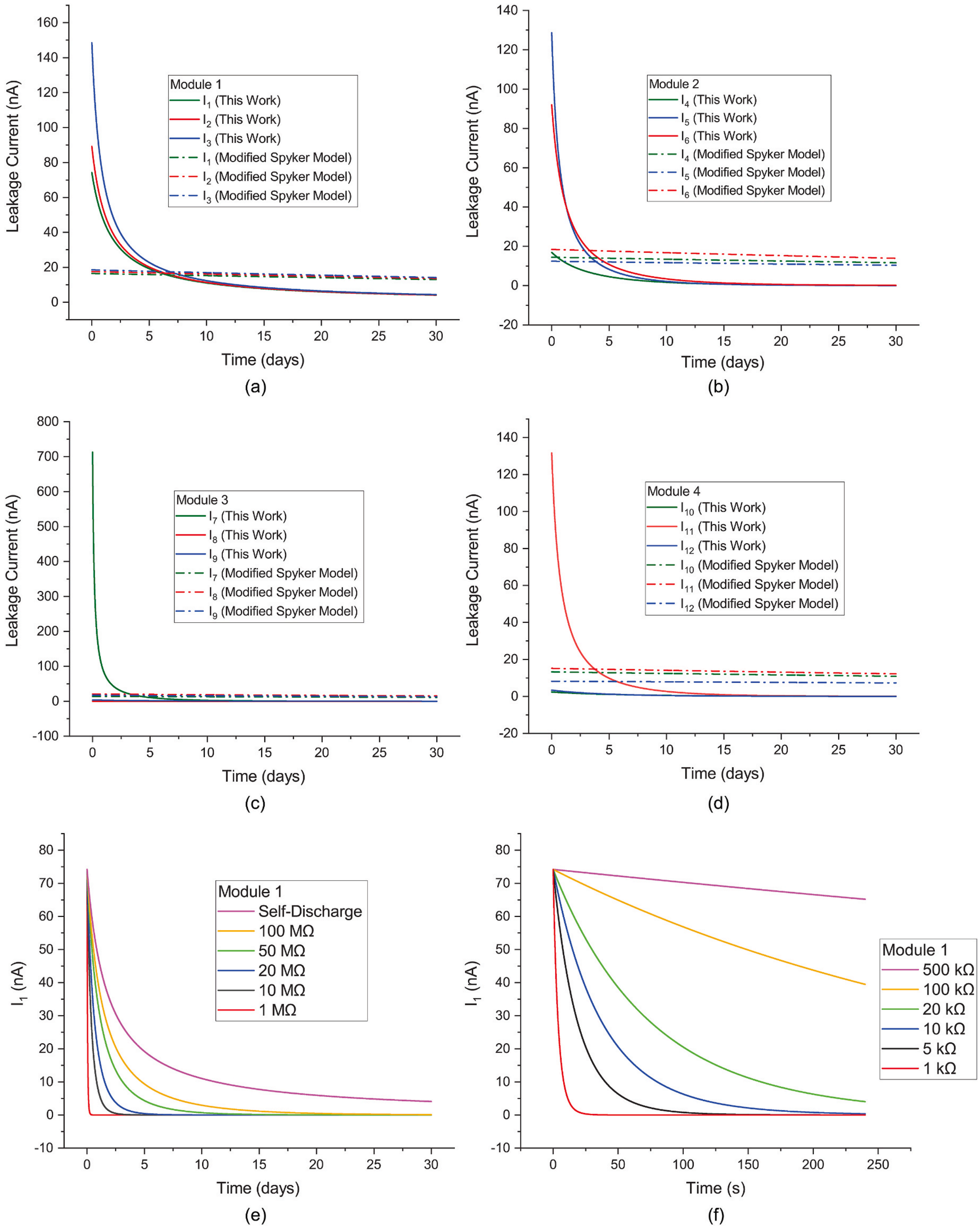


Fig. 8. a, b, c, d) Leakage behavior of SCs forming four energy modules using the proposed model and the modified Spyker model. e, f) The effect of the resistance load change on the leakage current of SCs.

energy storage technology, modelling the charging and discharging behavior of SCs in the form of energy modules also gives a good view into their performance in various applications as energy storage systems. The models reported in the literature have more RC network elements and branches and are complex for use in supercapacitor modules connected in series. These models are also not accurate to simulate the nonlinear self-discharge effect of the supercapacitors in long-term. In addition, exponential models using variable leakage resistance (VLR) have been published in the literature that have several separate exponential functions to model the self-discharge behavior of a single supercapacitor in the short-term (several hours). Accordingly, in order to simulate the self-discharge behavior of energy modules consisting of several supercapacitors connected in series for a long time (one month) using exponential models reported in the literature, a very large number of distinct exponential functions and parameters definition steps are required. Since simple versions are required to implement the models in practical applications, the models presented in the literature, despite having many RC network elements and parameter determination difficulties, are not suitable for long-term simulation of supercapacitor modules. To conclude, the reported approach in this work can simply model the SC internal charge/discharge redistribution and explain experimental results in long-term (31 days). Therefore, the work reported here provides a useful and applicable approach for testing the behavior of SC modules in energy storage systems and power management strategies. Potential applications of this type of SCs in which high power density and longevity are valuable features include energy autonomous Internet of Things (IoT), Energy-Harvesting Wireless Sensor Nodes and wearable self-charging power systems.

CRediT authorship contribution statement

Hamed Pourkheirollah: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Jari Keskinen:** Conceptualization, Methodology, Resources, Writing – review & editing. **Matti Mäntysalo:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision. **Donald Lupo:** Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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.

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