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Jong Kyu Lee and Jung Rag Yoon *

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Article

Effect of Electric Properties According to Volume Ratio of Supercapacitor and Battery Capacitor in Hybrid Energy Storage System

Jong Kyu Lee [1] and Jung Rag Yoon [1,*]

[1] R&D Center, SAMWHA CAPACITOR, 227 Gyeonggidong-ro, Korea
* Correspondence: yoonjungrag-@samwha.com

Abstract: The development of technology that combines supercapacitors and lithium-ion batteries by externally connecting them in parallel is ongoing. This study examines the correlation between the volume ratio and electrical characteristics of a cell made by internally connecting a battery capacitor with $Li_4Ti_5O_{12}$ as the anode active material and a supercapacitor in parallel. It was found that increasing the volume occupied by the battery capacitor in the cell led to increased cell energy and resistance, resulting in decreased output characteristics. Conversely, increasing the volume occupied by the supercapacitor in the cell led to a decrease in the IR drop during discharge and cell temperature when evaluating cycle characteristics with a current of 20C. The study also examined the behavior of the current distributed during the charging and discharging process based on the volume ratio of the supercapacitor and the battery capacitor. Analyzing the correlation between the volume ratio and electrical characteristics of supercapacitors and battery capacitors could potentially lead to the development of a new type of energy storage device.

Keywords: battery capacitor; supercapacitor; hybrid energy storage system; L-ion battery; $Li_4Ti_5O_{12}$

1. Introduction

Supercapacitors and lithium-ion batteries are widely used energy storage devices. Lithium-ion batteries achieve capacity by intercalating and deintercalating Li ions into and out of the crystal structure of the cathode and anode materials. On the other hand, supercapacitors achieve capacitance by adsorbing and desorbing ions from the electrolyte solution on the surface of activated carbon, which is an electrode material. The two energy storage devices have significant differences in their properties due to their different reaction mechanisms. Supercapacitors have low energy density, but their lifespan and output characteristics are significantly higher than those of lithium-ion batteries. Conversely, batteries have a much higher energy density compared to supercapacitors [1–10].

Supercapacitors have a voltage range of 0 to 2.7 volts, while the voltage range for lithium-ion batteries is typically between 3.0 to 4.2 volts. Supercapacitors have a high power density and can deliver high bursts of power. They also have a relatively short discharge time, typically on the order of a few seconds. Lithium-ion batteries, on the other hand, have a high energy density and can deliver power over a longer period of time, typically hours to days [11,12].

By combining supercapacitors and lithium-ion batteries, the resulting hybrid energy storage system can take advantage of the strengths of both technologies. The supercapacitors can provide high power density and fast discharge times, while the lithium-ion batteries can provide high energy density and longer discharge times. The voltage ranges of the two components can also be matched to allow for a smooth and efficient transfer of energy between the supercapacitors and lithium-ion batteries as needed.

Research to increase the lifespan of lithium-ion batteries by manufacturing a lithium-ion battery module and connecting supercapacitor modules in parallel to reduce the load on the lithium-ion battery is ongoing. This is because the reaction voltage of the individual cell of the supercapacitor and lithium-ion battery is different, so they are modularized and connected by matching their voltage. There is also a type of lithium-ion battery called a battery capacitor that is made of $Li_4Ti_5O_{12}$

(LTO) instead of graphite as the anode, which has excellent output and lifespan characteristics compared to graphite [13,14].

Most studies on combining supercapacitors and lithium-ion batteries are conducted at the module level, but battery capacitors have a similar voltage range to supercapacitors, allowing them to be connected in parallel between cells. This makes battery capacitor a candidate for transforming into a new type of energy storage device. By combining supercapacitors and battery capacitors, the system efficiency can be improved, and the lifetime characteristics can be improved by reducing the burden on the battery capacitor at high current. This results in a new energy storage device that is capable of both long-term energy storage and high power transmission. Additionally, the combination of supercapacitors and battery capacitors can provide high-performance energy storage while reducing the overall cost of an energy storage system [15–24].

It is important to note that the specific voltage range and discharge time for a hybrid energy storage system will depend on the specific components used, as well as the configuration of the system. However, in general, hybrid energy storage systems that combine supercapacitors and battery capacitors can offer improved performance and efficiency compared to using either technology alone.

In this study, we aim to investigate the improvement of system efficiency, reliability, performance, and cost-effectiveness by combining supercapacitors and battery capacitors in the same cell with a specific volume ratio.

2. Materials and Methods

2.1. Fabrication of Individual Cells

For the positive electrode of the battery capacitor, an electrode slurry was prepared by mixing two types of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (NCM) and $LiCoO_2$ (LCO) positive electrode active materials, with super-p serving as a conductive material and PVdF as a binder, in a mixing ratio of 87:6.5:6.5, and NMP used as a solvent. For the anode of the battery capacitor, a slurry was prepared using LTO as the active material and the same ratio of binder and conductive material as the cathode. The positive and negative electrodes were coated on etched Al foil with a thickness of 20 μm and subjected to a roll press to manufacture the positive and negative electrodes, with approximately 25% compression. The resulting electrodes were then formed into a jelly roll using a winding machine, dried at 145 °C for 48 hours, and impregnated with a 1.0M $LiPF_6$ + EC/DMC/EMC electrolyte solution to assemble the cell.

The supercapacitor utilized activated carbon as the electrode active material, super-P as the conductive material, and a binder consisting of a mixture of CMC, SBR, and PTFE. The electrode slurry was prepared with a ratio of 80:10:10 for the active material, conductive material, and binder, respectively. The electrodes were coated on etched Al foil with a thickness of 20μm and produced by a roll press with approximately 15% compression. The fabricated electrodes were then formed into a jelly roll using a winding machine, dried at 145°C for 48 hours, and impregnated with a 1.0M $TEABF_4$ + ACN electrolyte solution to assemble a cell.

2.2. Complex Cell Fabrication

The electrolyte of the battery capacitor uses the $LiPF_6$ salt, the supercapacitor uses the $TEABF_4$ salt, and other types of solvents are also utilized. To connect the battery capacitor and the supercapacitor in parallel within a single cell, it is necessary to insert a separation layer to prevent the mixing of electrolytes. Urethane was selected as the separation layer material, as it was determined to be suitable due to the absence of any reaction when immersed in both the battery capacitor electrolyte and the supercapacitor electrolyte.

Figure 1 presents a schematic diagram of the combination of a battery capacitor and a supercapacitor, showing the volume ratio and capacity ratio. The battery capacitor have a capacity that is approximately 17 times higher than that of the supercapacitors at the same volume, resulting

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in differences in capacity among cells depending on the volume ratio. Single battery capacitor and supercapacitors that have not been combined will also be compared to composite cells.

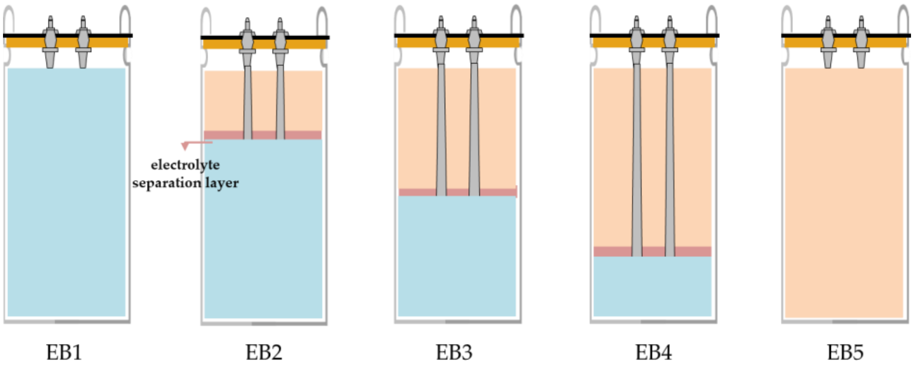

Figure 1. Schematic diagram of complex cell structure according to individual cell and volume ratio of battery capacitor and supercapacitor.

2.3. Cell Evaluation

The characteristics of battery capacitor, supercapacitors, and composite cells were evaluated by examining their charge/discharge current at 1.5 to 2.7V at room temperature using an Arbin charger/discharger. A long-term life evaluation was also conducted at room temperature, with a current of 20C. During the evaluation of cell life with a current of 20C, the temperature of the cell was measured using a thermal imaging camera. To assess the current distribution to the battery capacitor and the supercapacitor during the charging and discharging process of the composite cell, it was measured using an oscilloscope.

Table 1. The properties of complex cell structure according to individual cell and volume ratio of battery capacitor and supercapacitor.

	EB1	EB2	EB3	EB4	EB5
Supercapacitor (F)	872.3	654.3	436.2	218.0	-
Battery capacitor (F)	-	3801.6	7603.2	11404.8	16203.0
Volume ratio occupied by EDLC (%)	100	75	50	25	0
Capacity ratio occupied by EDLC (%)	100	14.7	5.4	1.9	0

3. Results

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

Figure 2 shows the capacitance and resistance of the individual battery capacitor and supercapacitor cells, as well as the composite cell, measured by applying a current of 1A at 2.7~1.5V. The composite cell's capacity decreases as the volume ratio of the battery capacitor increases because the battery capacitor's capacity is about 17 times larger than that of the supercapacitor. Additionally, the resistance of the composite cell decreases as the volume of the supercapacitor increases since the supercapacitor's resistance is 25% of that of the battery capacitor.

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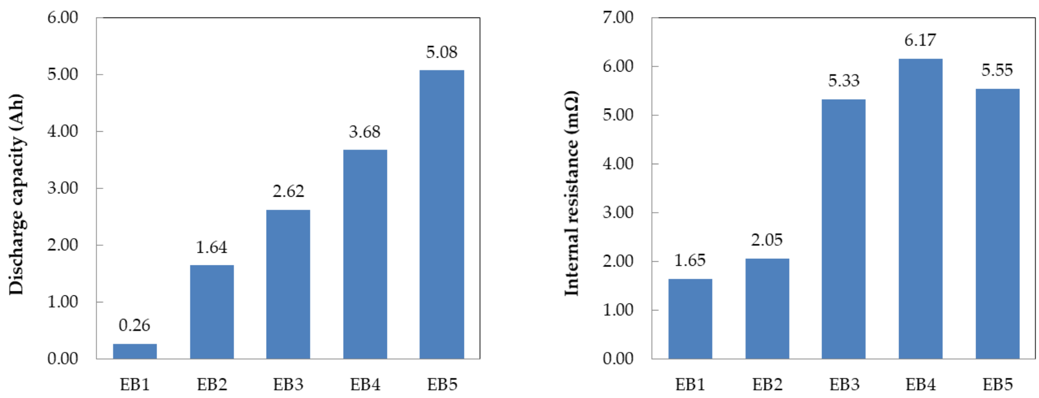

Figure 2. The cell capacity and resistance according to the volume ratio of battery capacitor and supercapacitor in a composite cell.

Figure 3 illustrates the discharge curves of the individual battery capacitor and supercapacitor cells, as well as the composite cells. Supercapacitors exhibit a linear discharge curve that depends on the voltage since ions in the electrolyte are adsorbed/desorbed on the surfaces of the anode and cathode electrodes, resulting in low voltage drop due to low resistance. Conversely, battery capacitor have a flat section in their discharge curve since Li ions intercalate/deintercalate from the positive and negative electrode materials at a specific voltage, instead of a linear discharge curve [25]. The initial voltage during discharge increases as the volume ratio of the supercapacitor increases in the composite cell. This occurs because the battery capacitor changes to a supercapacitor discharge curve in the initial discharge voltage range due to low energy.

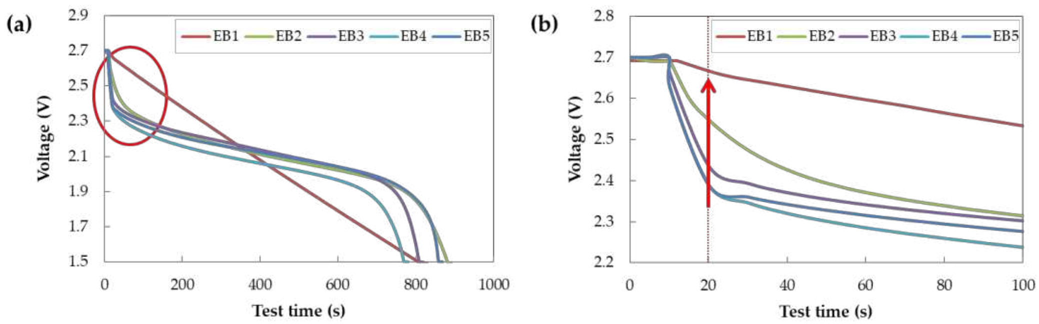

Figure 3. The discharge curve according to the volume ratio of battery capacitor and supercapacitor in a composite cell.

Figure 4 presents the rate of change in capacity and resistance of the individual Battery capacitor and supercapacitor cells, as well as the composite cells, with respect to the applied current. The capacity change rate tended to decrease as the current increased, and the rate of change in resistance decreased, except for the supercapacitor cells alone. It was confirmed that the capacity change rate increased as the volume ratio of the supercapacitor increased in the composite cell, where a battery capacitor and a supercapacitor were combined. The high output characteristics of the supercapacitor are believed to assist the output characteristics of the battery capacitor at high current.

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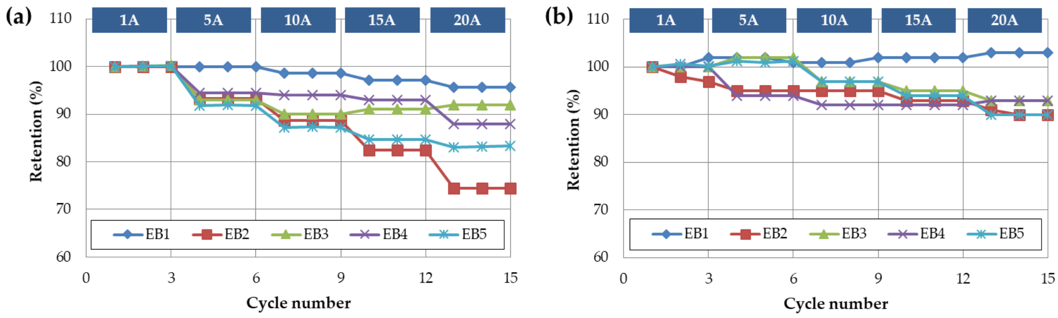

Figure 4. The c-rate properties according to the volume ratio of battery capacitor and supercapacitor in a composite cell ((a) capacity, (b) internal resistance).

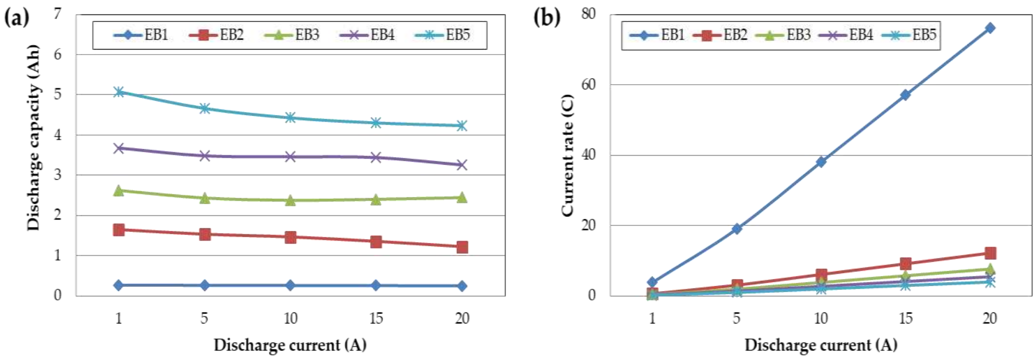

Figure 5. The cell capacity and current rate according to current density.

The individual and composite cells of the battery capacitor and supercapacitor were manufactured to the same size and assembled with different internal volume ratios. When evaluated at a charge/discharge current of 1~20A, the current received per volume is the same. However, when compared by the cell capacity, a cell made of only supercapacitors receives 76.09C at 20A, whereas a battery capacitor receives 3.94C. Even though the received current per volume is the same, since the capacity differs according to the volume ratio of the composite cell, the current received in terms of capacity may vary significantly.

In order to evaluate the lifespan characteristics of the battery capacitor and supercapacitor individual cells and composite cells, a life evaluation was conducted at room temperature with a current of 20C, as shown in Figure 6. The results showed that the number of cycles at which the capacity retention rate is less than 80% compared to the initial capacity during charging/discharging with the battery capacitor 20C is about 4200 cycles. However, when the supercapacitor is added to the composite cell according to the volume ratio, the number of cycles at which the capacity retention rate is less than 80% increases. One of the main factors contributing to the increased lifespan of the battery capacitor combined with a supercapacitor is the amount of heat generated from the cells.

The temperature of the cell during the cycle evaluation was measured with a thermal imaging camera, and is shown in Figure 7. During the life evaluation, the surface temperature of the cell using only the battery capacitor was measured at 43 to 48 °C, while the temperature at the jelly roll stage was estimated to be higher than 60°C, indicating a temperature difference of approximately 15°C between the surface and inside of the cell. Since the temperature of the cell is one of the biggest factors affecting its lifespan characteristics, combining it with the supercapacitor led to a decrease in temperature during the charge/discharge process, and consequently, an improvement in lifespan characteristics.

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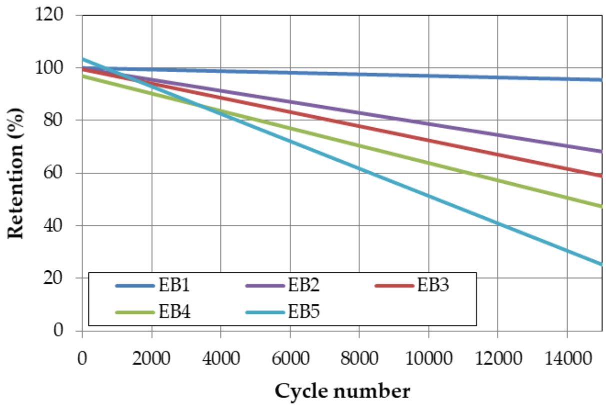

Figure 6. The cycle properties according to the volume ratio of battery capacitor and supercapacitor in a composite cell.

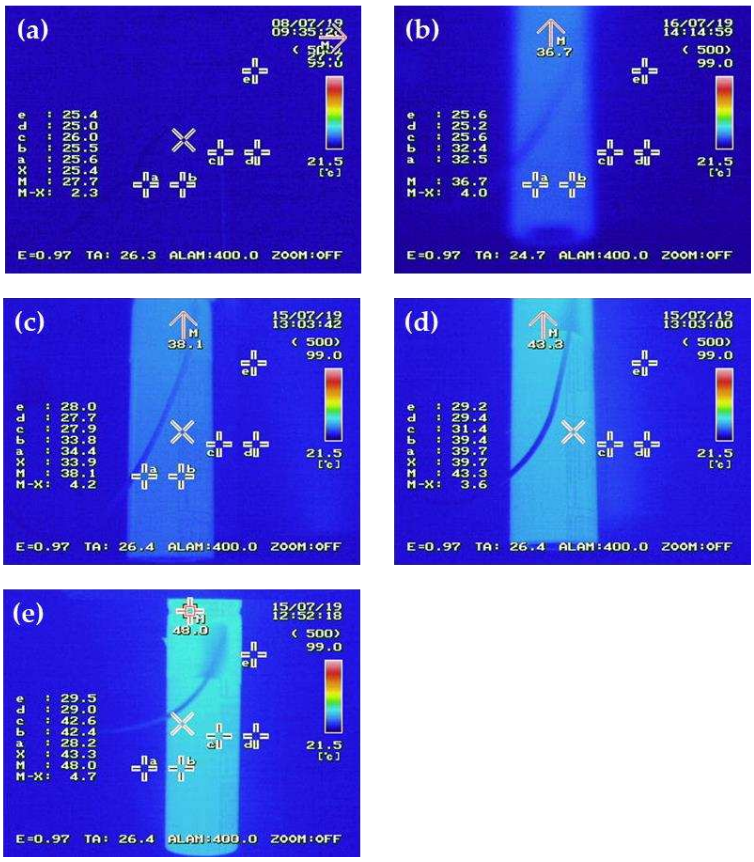

Figure 7. The cell temperature according to cycle measurement: (a) EB1, (b) EB2, (c) EB3, (d) EB4, (e) EB5.

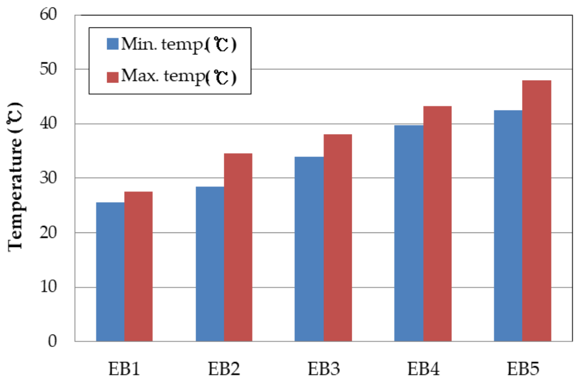

Figure 8. The maximum and minimum temperature of the composite cell measured during cycle measurement.

To investigate the current behavior during charging and discharging of a parallel-connected battery capacitor and supercapacitor, we measured individual currents using an oscilloscope and presented the results in Figure 9 and Table 2. During charging, the supercapacitor initially accepted current at a high rate, and the charging current gradually decreased over time. In contrast, the battery capacitor did not initially accept the charging current, but we confirmed that it increased over time. According to the current distribution law, initially most of the charging current flowed into the supercapacitor due to its low resistance, but as the supercapacitor became charged, the charging current shifted towards the battery capacitor. By absorbing the initial surge of current during charging and discharging, the supercapacitor can reduce the damage to the battery capacitor, which gradually receives the current [26].

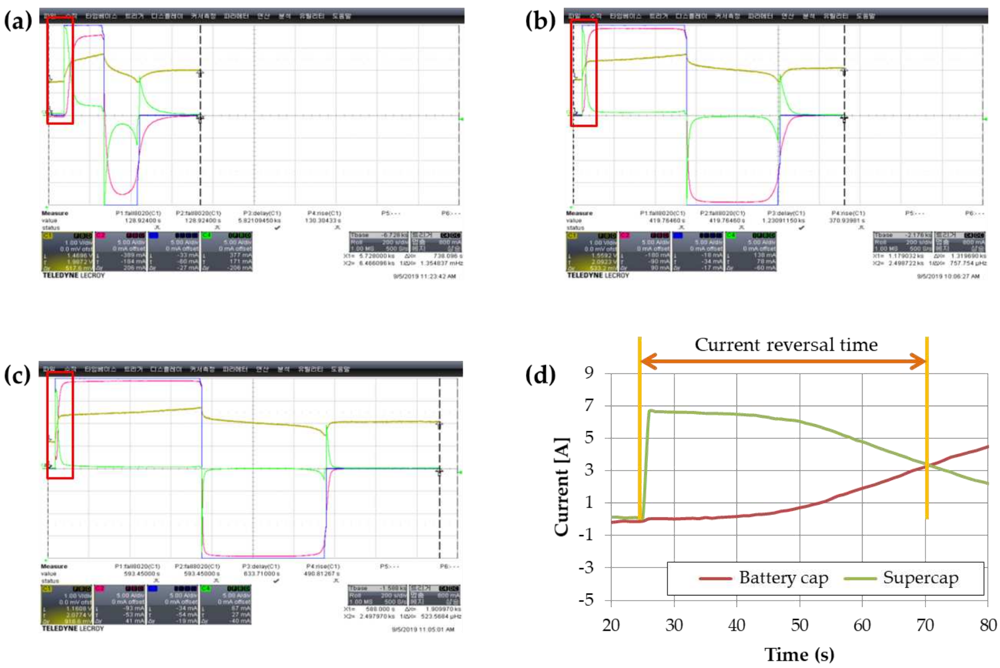

Figure 9. The current distributed between the battery capacitor and supercapacitor when charging and discharging the composite cell: (a) EB2, (b) EB3, (c) EB4, (d) Enlarged part of current behavior.

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Table 2. Distributed current properties of battery capacitors and supercapacitors when charging and discharging complex cells.

Item	EB2		EB3		EB4	
	Super capacitor	Battery capacitor	Super Capacitor	Battery capacitor	Super Capacitor	Battery capacitor
Percentage of supercap in total capacity (%)	14.7	85.3	5.4	94.6	1.9	98.1
Initial current (A)	19.56	0.44	18.86	1.14	17.65	2.32
Initial current rate (%)	97.8	2.2	94.3	5.7	88.2	11.8
Time for the current to reverse (s)	13		20		45	

Figure 10 presents the electrical characteristics of the composite cell as a function of the volume ratio of the supercapacitor and battery capacitor, based on our measurements. As the volume occupied by the supercapacitor increases in the composite cell, the capacity, resistance, and energy density per unit volume tend to decrease, while the lifespan, output characteristics, and cost for energy storage tend to increase. Due to the different characteristics of the supercapacitor and battery capacitor, the composite cell exhibits various electrical characteristics depending on the volume ratio. Consequently, it is possible to design a new type of energy storage device with complementary characteristics by adjusting the volume ratio of the components.

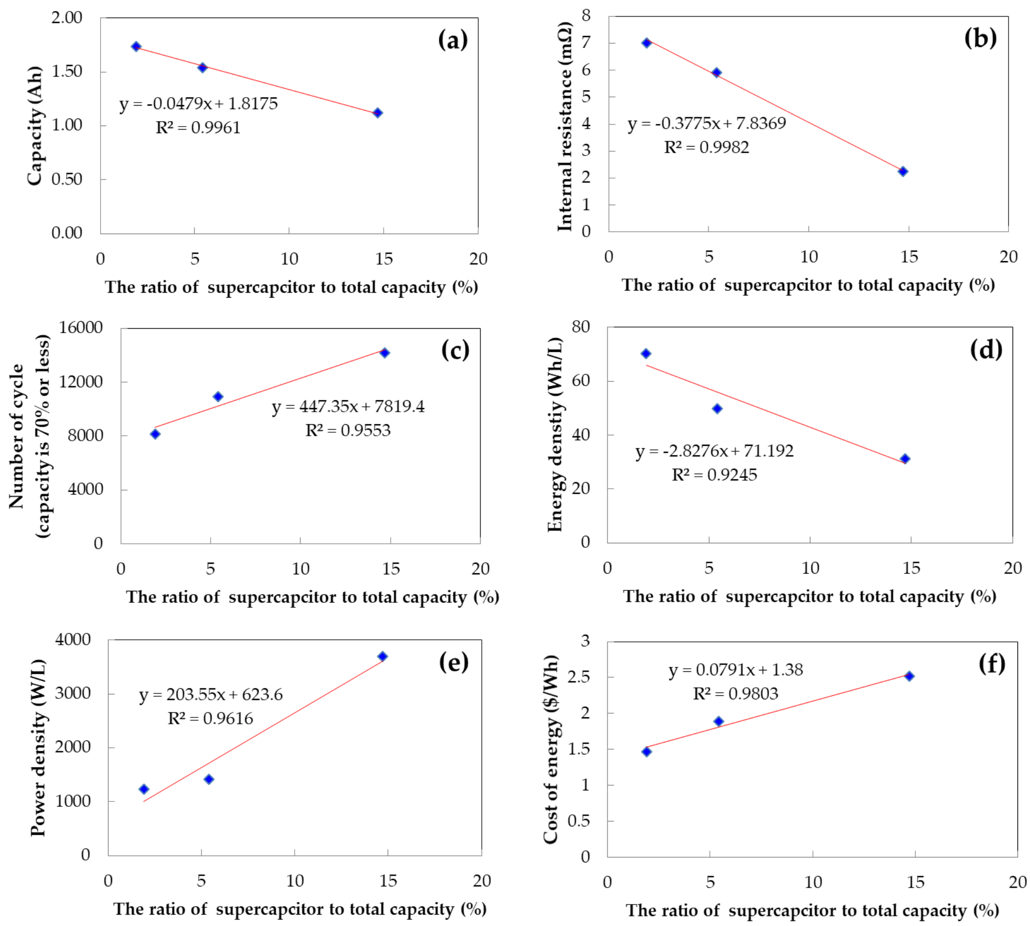

Figure 10. The trend of characteristics according to the volume ratio of battery capacitor and supercapacitor in composite cell.

4. Discussion

The conclusion of the dissertation proposes the development of a new type of energy storage device through internal parallel connection of two different types of energy storage devices. The study shows that supercapacitors and battery capacitors can complement each other's characteristics when compounded, with the battery capacitor affecting energy improvement and the supercapacitor affecting resistance and lifespan characteristic improvement. The volume ratio of the two storage devices affects the characteristics of the complex cell, and the study allows for the quantification of the capacity, resistance, lifespan, energy density, power density, and cost of a composite cell based on the volume ratio. This enables the design of new energy storage devices suitable for applications and will play an important role in the field.

Author Contributions: Conceptualization, J. K. L and J. R. Y.; methodology, J. K. L and J. R. Y.; software, J. K. L.; validation, J. K. L and J. R. Y; formal analysis, J. K. L and J. R. Y.; investigation, J. K. L and J. R. Y.; resources, J. K. L and J. R. Y.; data curation, J. K. L and J. R. Y.; writing—original draft preparation, J. K. L.; writing—review and editing, J. K. L and J. R. Y.; visualization, J. K. L.; supervision, J. K. L and J. R. Y.; project administration, J. K. L and J. R. Y.; funding acquisition, J. K. L and J. R. Y. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data available on request.

Conflicts of Interest: The authors declare no conflict of interest.

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