INDONESIAN JOURNAL OF INNOVATION AND APPLIED SCIENCES (IJIAS)
Journal Homepage: https://ojs.literacyinstitute.org/index.php/ijias
ISSN: 2775-4162 (Online)
Research Article

Volume 1	Issue 3	October (2021)	DOI: 10.47540/ijias.v1i3.303	Page: 208 – 218

Comparative Analytical Modeling and Performance Investigation of Graphene-Based Super Capacitor with Four Traditional Batteries

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ARTICLE INFO

Keywords: Batteries, Comparative Study, Graphene, Lithium-Ion, Dynamic Model.

Received : 26 July 2021
Revised : 25 September 2021
Accepted : 12 October 2021

ABSTRACT

Graphene, a magical development of 2004, has revolutionized today's energy storage technologies. It is nothing but a graphite two-dimensional (2D) allotropic pure carbon layer which is derived from a three-dimensional (3D) shape. Since batteries have been the most common storage device from the invention of the first electrical battery by an Italian physicist Alessandro Volta in 1799 A.D but batteries offer many drawbacks, such as length, weight, poor transient response, low power density, and high internal resistance. In this contrast, the impressive and unique properties of graphene supercapacitor such as high peak current, high surface area, high electrical conductivity, low internal resistance, high load current, long life cycle, high power density, low-temperature charging, and discharging make graphene supercapacitor a replacement of traditional energy storage devices and sets trend for the future. This analytical comparative analysis presents an overview between four traditional batteries and graphene-based supercapacitor. For this regard, dynamic models, modeling equations, and an integrated simulation model for batteries and graphene-supercapacitors under MATLAB/Simulink® 2020a environment is developed. In addition, the effect of temperature on battery output and graphene-supercapacitor is also addressed.

INTRODUCTION

Royal Swedish Academy of Science honored Noble Prize in Physics to Andre K. Geim and Konstantin S. Novoselov in 2010 for the efficient development, isolation, identification, and characterization of Graphene (Novoselov, et al., 2004; The Royal Swedish Academy of Sciences, 2010). Graphene is a 3-Dimensional (3D) isolated graphite layer to which 2-Dimensional (2D) honeycomb lattices are tightly packed (Novoselov, et al., 2005).

Compared to the single atom diameter, Graphene layers are roughly 1/10 mm thin (graphenea.com, 2021). Three trivalent covalent bonds form graphite between the C-C atoms, where the length of the bond between the two carbon atoms is around 1.42A° (Geim & Novoselov, 2007). To form graphite, graphene layers combine with an internal planner spacing of 0.335nm (Khan, et al., 2020). Due to the unusual zero overlap difference between valance and conduction band, graphene is often called Unimetal (Mollik, et al., 2019; Prasad, et al., 2019). The young graphene modulus is approximate ~ 1 tera pascal. That makes graphene the stiffest material ever known to man. In addition, electron mobility up to 2500 (cm2)/vs (Baboselac, et al., 2017; Hinov, et al., 2018) is seen.

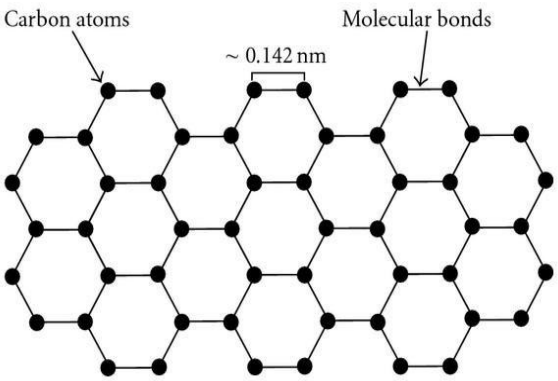

Figure 1. Inner Structure of Graphene

Graphene is a Wonder material, the electrical conductivity of graphene is 1×106 times the copper conductor while its mobility is 1×103 times the silicon material (Singh & Kumar, 2017), thermal conductivity (3000-5000 W⁄Mk times graphite, diamond, copper & silver) (Zuo, et al., 2017), also known as "high temperature". Since conductivity is 133ºC (Kurniawan, et al., 2016), transparency (2.3%) (Haizhou, 2017), and strength (strongest ever known material, which is 40 times stronger than diamond, 300 times than A36 structural steel). This enables it to be used in the design and manufacture of various field applications, such as batteries, solar panels, fuel cells, supercapacitors, sensors, photodetectors, coatings, loudspeakers, radiation shields, thermal control, cloaking, lubrication, water purification, etc.

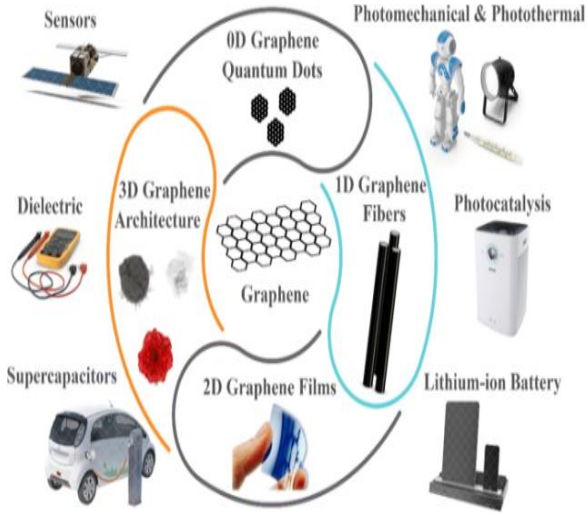

Figure 2. Different applications of Graphene

Pollution problems and environmental effects as a long-term goal have led green energy a necessity of today's green world. Nowadays, more research is going on minimization of the exhaust of carbon dioxide. Renewable energy sources storage batteries are a promising solution for environmental and economic benefits.

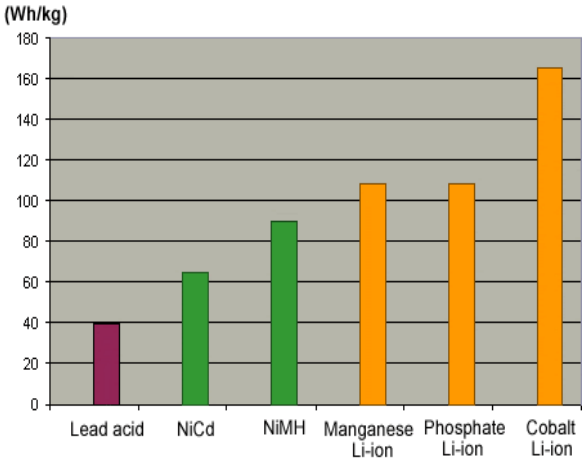

Figure 3. Energy content by different batteries

Graphene supercapacitor or ultra-capacitor has capacitance better capacitance than an ordinary capacitor, electrical double-layer capacitors (EDLC). There are 3 types of capacitors Double layer capacitor, Hybrid capacitance, and Pseudo-capacitor. Below fig 4 represents the energy and power density of energy storage devices.

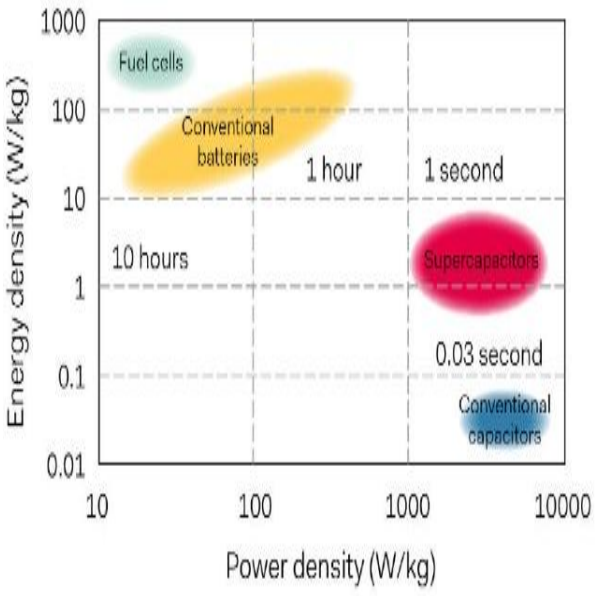

Figure 4. Energy & power densities of different storage devices

Graphene Supercapacitor has electrolyte ions to produce a high charge as compared to standard capacitors (Poonsuk & Pongyupinpanich, 2016).

Table 1. Comparison of general characteristics between the battery and the supercapacitor Graphene.

Characteristics	Batteries	Graphene-Based Supercapacitor
Charge Time	0.3h-3h	1~30s
Discharge Time	1~5	1~30s
Energy Density	20~100	1~10
Power Density	50~200	7000-18000
Efficiency	70% - 85%	85% - 90%
Cycle life	200-1000	$10^6 - 10^8$

Source: Barua, S., et al. (2015).

The global energy paradigm is rapidly changing from fossil fuel to renewables. For the development of the best energy storage device, significant effort has been made from Lithium-Ion batteries, supercapacitors to Lithium-Ion capacitors.

This research aims to observe the performance investigation-based comparative analysis for dynamic modeling, equations modeling and simulation modeling for batteries and grapheme-supercapacitors under MATLAB/simulink® 2020a environment.

METHODS

Graphene-Based Supercapacitor and Other Energy Storage System Analytical Comparison

The specific energy density of the supercapacitor with graphene-based electrodes is approximately 85.6Wh/kg, while 136 Wh/kg at 80 ^{0}C is estimated at a current density of 1 A/g. Its high capacitance of 550 F/g and real surface area of 2675 m^2/g is a significant property of graphene.

Table 2. Energy density and power density comparisons.

Storage Device	Maximum Specific Energy Density (Wh/kg)	Maximum Specific Power Density (Wh/kg)
Alkaline Batteries	85	50
Lithium-Ion Batteries	250	350
Graphene Based Supercapacitor	33	1184

Battery Model in MATLAB/Simulink® 2020a

MATLAB/Simulink® 2020a is used to model batteries for lead-acid, lithium-ion, nickel-cadmium, and nickel-metal hydride batteries. Below is the parameterized model representation of batteries.

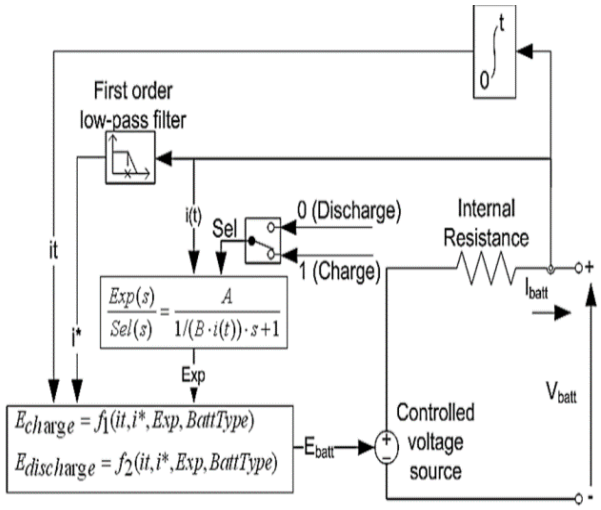

Figure 5. The generic dynamic model of batteries

The following Stern equation and Tafel equation are implemented by the Supercapacitor block in MATLAB [21, 22]:

$$N = \frac{NN_S QX_2}{N_P N^2 \varepsilon\varepsilon_\circ A} + \frac{NN_S 2RT}{F} \alpha r \sinh\left(\frac{Q}{N_P N^2 A\sqrt{8RT\varepsilon\varepsilon_\circ C}}\right)$$

$$-i_C(t) = Ai_0 exp\left(\frac{\alpha F\left(\frac{V}{N_S} - \frac{V_{max}}{N_S} - \Delta V\right)}{RT}\right)N$$

For graphene-based supercapacitor modeling, the two general equations for traditional supercapacitors are used.

Where parameters are represented:

N = Number of layers of electrodes

N_S = Number of series supercapacitor

N_P = Number of parallel supercapacitors

Q = Electric charge in colomb

ε = Permittivity of material in coloumb

ε = Permittivity of free space -8.85 x 10^{12} F/m

A = Interfacial area between electrodes and electrolyte (m^2)

R = Ideal gas constant -5.189 x 10^{19} eVK^{-1} mol^{-1}

X_2 = Helmholtz layer length (m)

T = Operating temperature (in Celsius)

α = Charge transfer coefficient, Tafel equation (0< α <1)

r = Molecular radius =X_2

N_A = Avagado constant -6.02214129 x 10^{23} mol^{-1}

i_0 = Exchange current density = $\frac{if}{A} Am^2$

if = Leakage current in Ampere

V_{max} = Surge voltage – Maximum voltage of the supercapacitor (V)

V = Supercapacitor rated voltage

ΔV = Over potential (V)

It is possible to measure the supercapacitor State of charge (SOC) using:

$$SOC = \frac{Q_{init} - \int_0^t i(\tau)d\tau}{QT} \times 100$$

Hypotheses taken for modeling are:

1. No impact on temperature.
2. No ageing results.
3. Cell balancing has not been planned.

The Charging Model Overview

1. Lead-Acid

$$E_{batt} = E_\circ - K\frac{Q}{it–0.1.Q}.^{i^*} - K\frac{Q}{Q-it}.it + Exp(t)$$

2. Lithium-Ion

$$E_{batt} = E_\circ - K\frac{Q}{it–0.1.Q}.^{i^*} - K\frac{Q}{妖-it}.it + Aexp(-B\cdot it)$$

3. NiMH and NiCd

$$E_{batt} = E_\circ - K\frac{Q}{|it|–0.1.Q}.^{i^*} - K\frac{Q}{Q-it}.it + Exp(t)$$

Different Batteries Mathematical Equations

1. Lead Acid Model

Discharge Model (i*>0)

$$f_1(it, i^*, i, Exp) = E_\circ - \text{.}\mathcal{J}\cdot\frac{Q}{Q-it}\cdot i^*K\cdot\frac{Q}{Q-it}it + Laplace^{-1}\left(\frac{Exp(s)}{Sec(s)}\cdot 0\right)$$

Charge Model (i*<0)

$$f_2(it, i^*, i, Exp) = E_\circ - K\cdot\frac{Q}{it+0.1Q}\cdot i^* - K\cdot\frac{Q}{Q-it}\cdot it + Laplace^{-1}\left(\frac{Exp(s)}{Sec(s)}\cdot\frac{1}{s}\right)$$

2. Lithium-Ion Model

Discharge Model (i*>0)

$$f_1(it, i^*, i) = E_\circ - K\cdot\frac{Q}{Q-it}\cdot i^* - K\cdot\frac{Q}{Q-it}\cdot it + Aexp(-B, it)$$

Charge Model (i*<0)

$$f_2(it, i^*, i) = E_\circ - K\cdot\frac{Q}{it+0.1Q}\cdot i^* - K\cdot\frac{Q}{Q-it}\cdot it + Aexp(-B, it)$$

3. Nickel-Cadmium & Nickel-Metal-Hydride Model

Discharge Model (i*>0)

$$f_1(it, i^*, i, Exp) = E_\circ - K\cdot\frac{Q}{Q-it}\cdot i^* - K\cdot\frac{Q}{Q-it}\cdot it + Laplace^{-1}\left(\frac{Exp(s)}{Sec(s)}\cdot 0\right)$$

Charge Model (i*<0)

$$f_2(it, i^*, i, Exp) = E_\circ - K \cdot \frac{Q}{|\, it \,| + 0.1Q} \cdot i^* - K \cdot \frac{Q}{Q - it} \cdot it + Laplace^{-1}\left(\frac{Exp(s)}{Sec(s)} \cdot \frac{1}{s}\right)$$

When:
$E_\circ$ = Battery Constant Voltage (V)
Exp(s) = Exponential Zone dynamic (V)
Sel(s) = Battery Mode
Sel(s) = 0 (Represent battery discharging)
Sel(s) = 1(Represent battery charging)
K = Polarization Constant

$$\left(AH^{-1}\right) = \frac{\left(E_{Full} - E_{Nom} + A\left(exp(-B, Q_{Nom}) - 1\right) \cdot \left(Q - Q_{Nom}\right)\right)}{Q_{Nom}}$$

Q = Maximum battery capacity (Ah)
it = Extracted capacity (Ah)
A = Exponential voltage (V)
B = Exponential capacity (Ah^{-1})
i = Battery current (A)

RESULTS AND DISCUSSION

Discharging Characteristics of Batteries after Simulation

For various batteries, the discharge characteristics were analyzed. Three sections form a standard discharge curve: Discharge curve, Nominal area, and Exponential area.

Lead Acid Battery

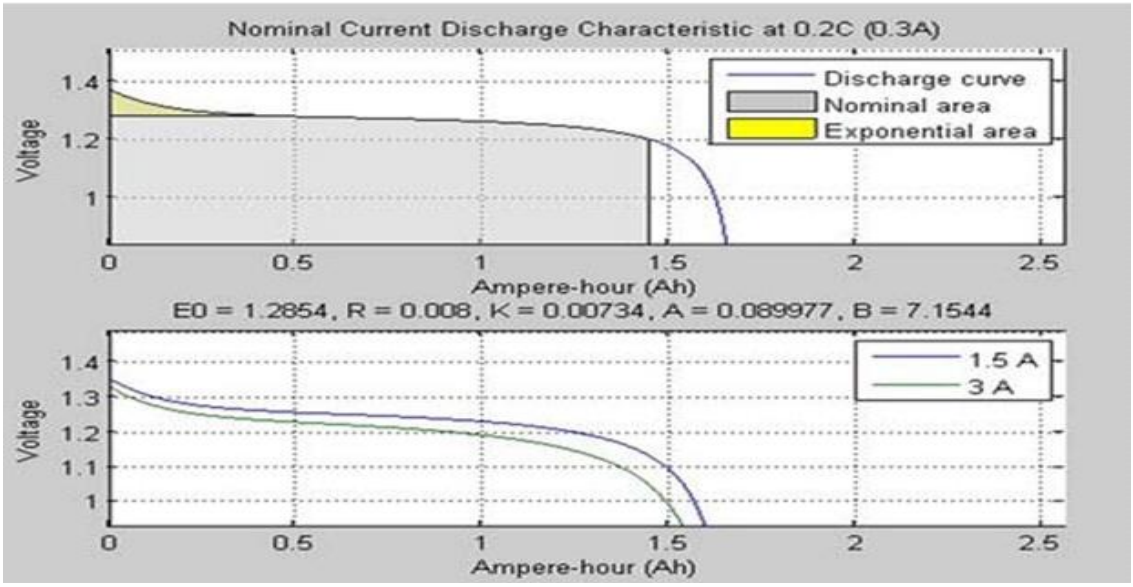

Figure 6. Lead Acid Battery Discharge Characteristics

Lithium-Ion Battery

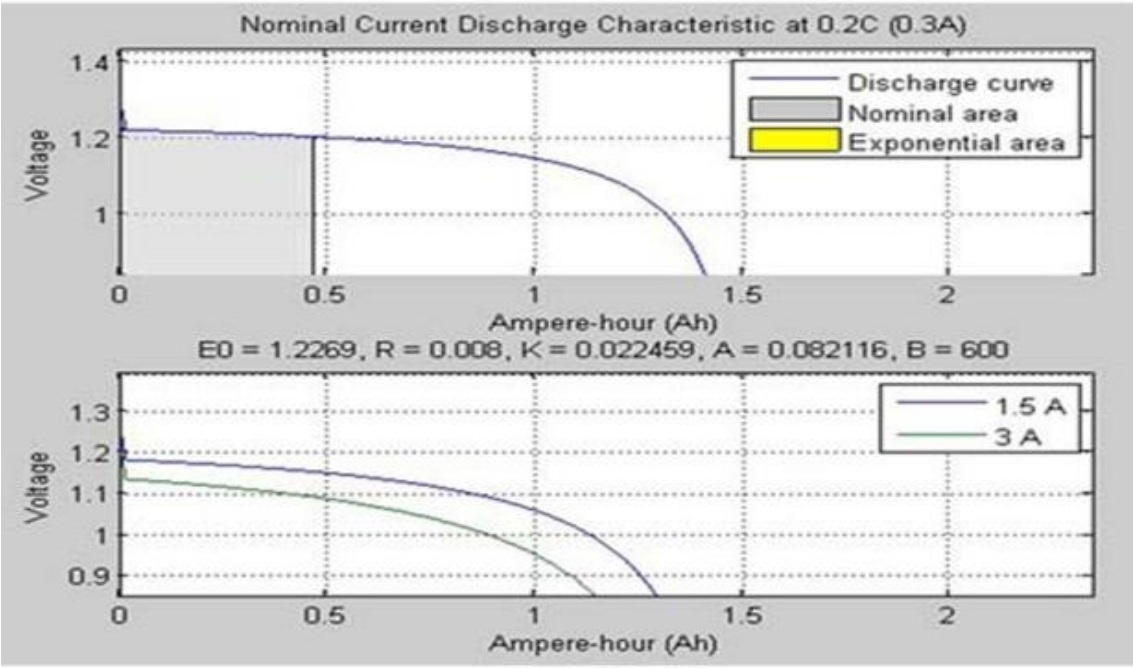

Figure 7. Characteristics of Lithium-Ion Battery Discharge

Nickel-Cadmium Battery

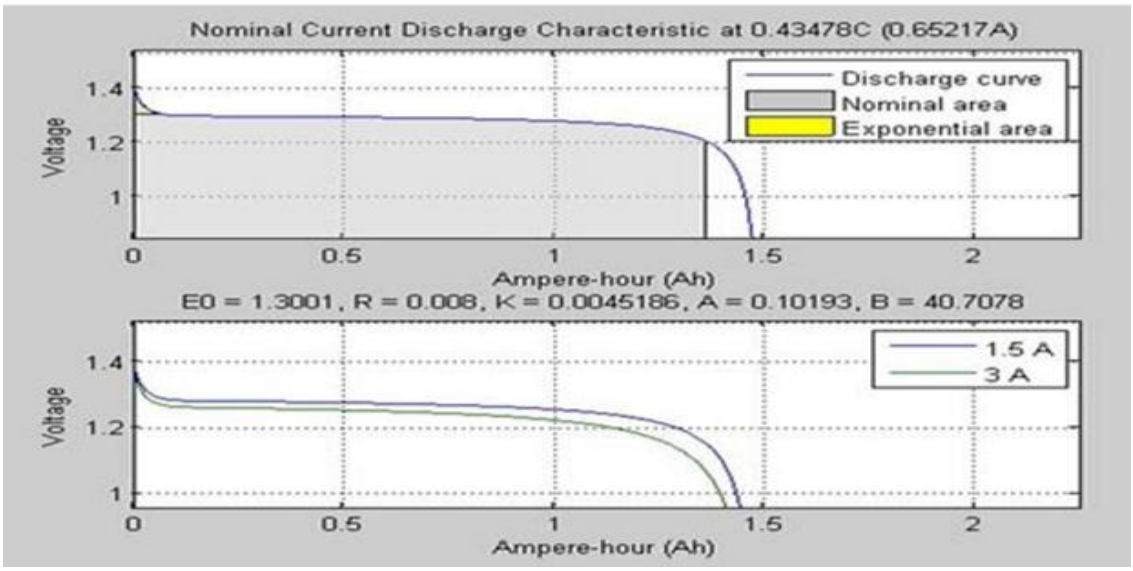

Figure 8. Nickel Cadmium Battery Discharge Characteristics

Nickel-Metal-Hydride

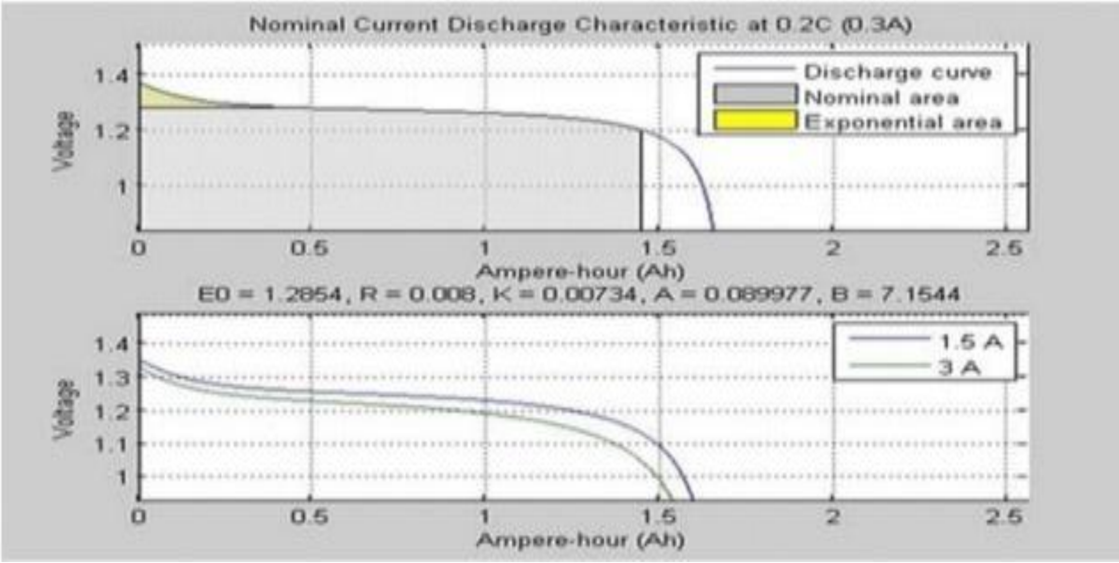

Figure 9. Nickel Metal Hydride Battery Discharge Characteristics

When the battery current is negative, the battery will display the charge functionality. Using the following equations.

$$OCP_{pos} = 4.19829 + 0.0565661\tanh(-14.556y + 8.60942) - 0.0275479\left(\frac{1}{((0.998432-y)^{0.492465})} - 1.90111\right) - 0.157123e^{(-0.04738y^{8})} + 0.810239e^{(-40(y-0.133875))}$$

Range of y is: 0.4<y<0.9981

$$OCP_{neg} = \frac{(1.997 + 2.472x)}{1 + 31.823x}$$

$$OCP_{cell} = OCP_{pos} - OCP_{neg}$$

$$V_{cell} = OCP_{cell} - \eta_V$$

$$SOC = \frac{x - x_{min}}{(x_{max} - x_{min})}$$

And,

$$y = (1 - SOC) \times (y_{max} - y_{min}) + y_{min}$$

If cathode as limiting electrode, then

$$SOC = \frac{y - y_{min}}{(y_{max} - y_{min})}$$

Faraday's law is used to determine State of Charge (SOC) of individual electrode, the series batteries net mass is given by the formula,

$$m_b = W_{Li-cell} \times n_{Li}$$

Finally, the energy of battery in joules

$$= \left(\int_0^1 V_{cell} \times n_{Li} \times I_{batt}\right)$$

Where:

y=Intercalation coefficient of the positive electrode

x=Intercalation coefficient of the negative electrode

OCP_{pos}= Open circuit potential of positive electrode in Volts

OCP_{neg}= Open circuit potential of negative electrode in Volts

OCP_{cell}= Open circuit potential of individual cell in Volts

V_{cell} = Individual lithium ion cell voltage in Volts

n_{Li}=Number of lithium ion cells

$W_{Li\text{-}cell}$= Mass of one lithium ion cell voltage in Volts

$$SOC = State\ of\ charge = 100\left(1 - \frac{1}{Q}\int_0^t i(t)dt\right)$$

Impact of Temperature on the Batteries and Graphene-Based Supercapacitor Charging and Discharging Efficiency Parameters

1. Comparative study of temperature-dependent and independent batteries of lithium-ion A & B

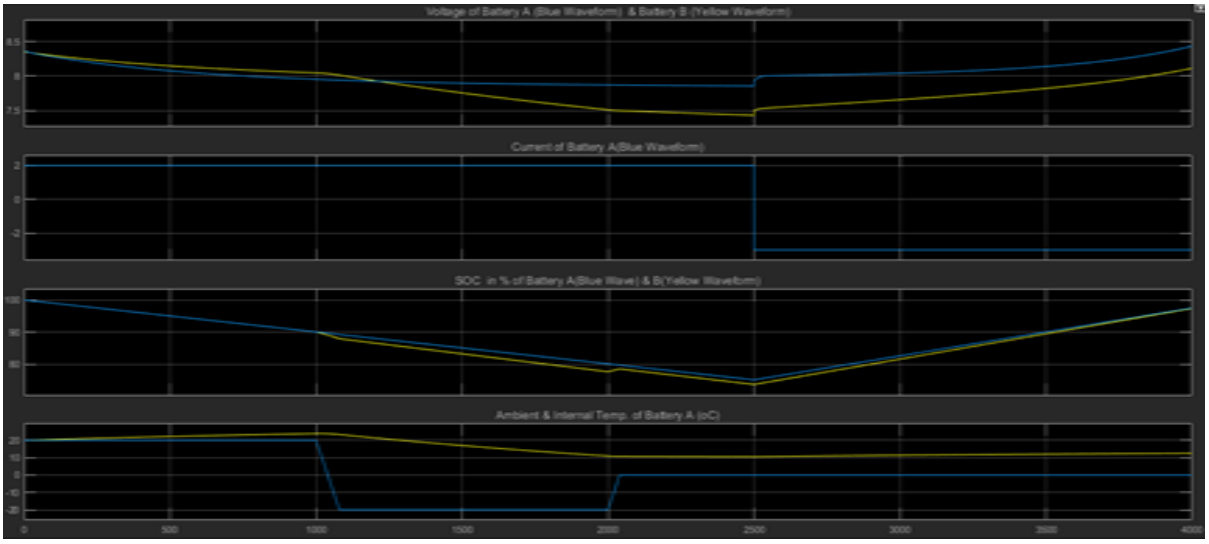

Figure 10. Effect of temperature on temperature-dependent lithium-ion batteries A and temperature-dependent charging and discharging characteristics for lithium-ion batteries B

2. Comparative study of the independent lead-acid battery C & temperature-dependent battery A

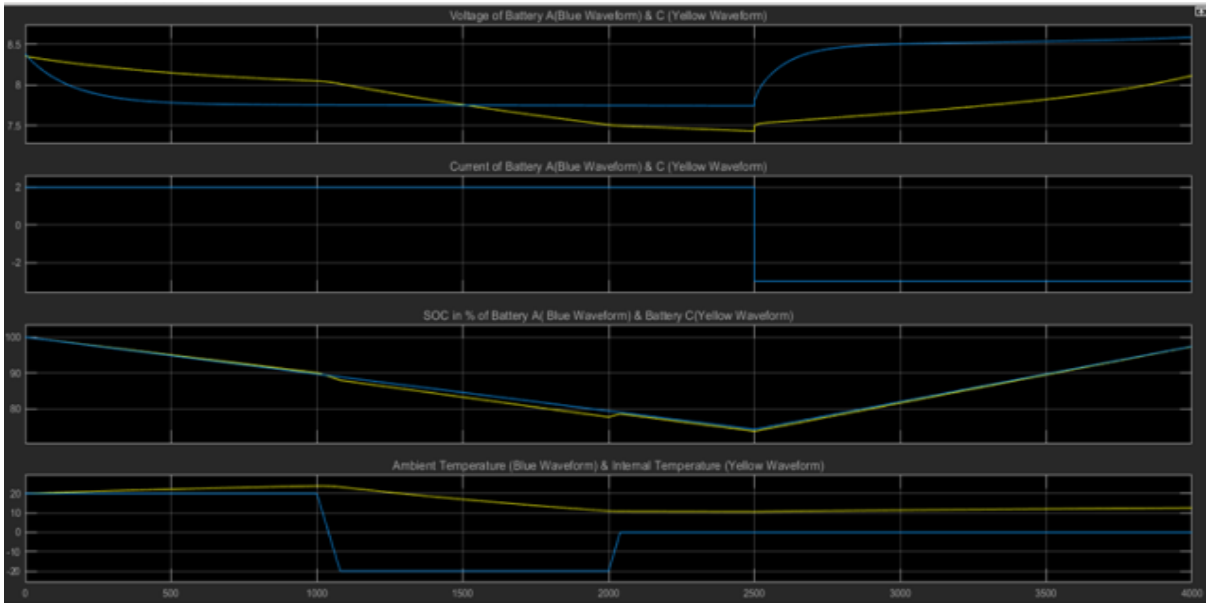

Figure 11. Effect of temperature on temperature-dependent charging and discharging characteristics of lithium-ion battery A & temperature-dependent lead-acid battery C

3. Analytical Comparison between temperature-dependent lithium-ion battery & Independent Nickel-Cadmium Battery D

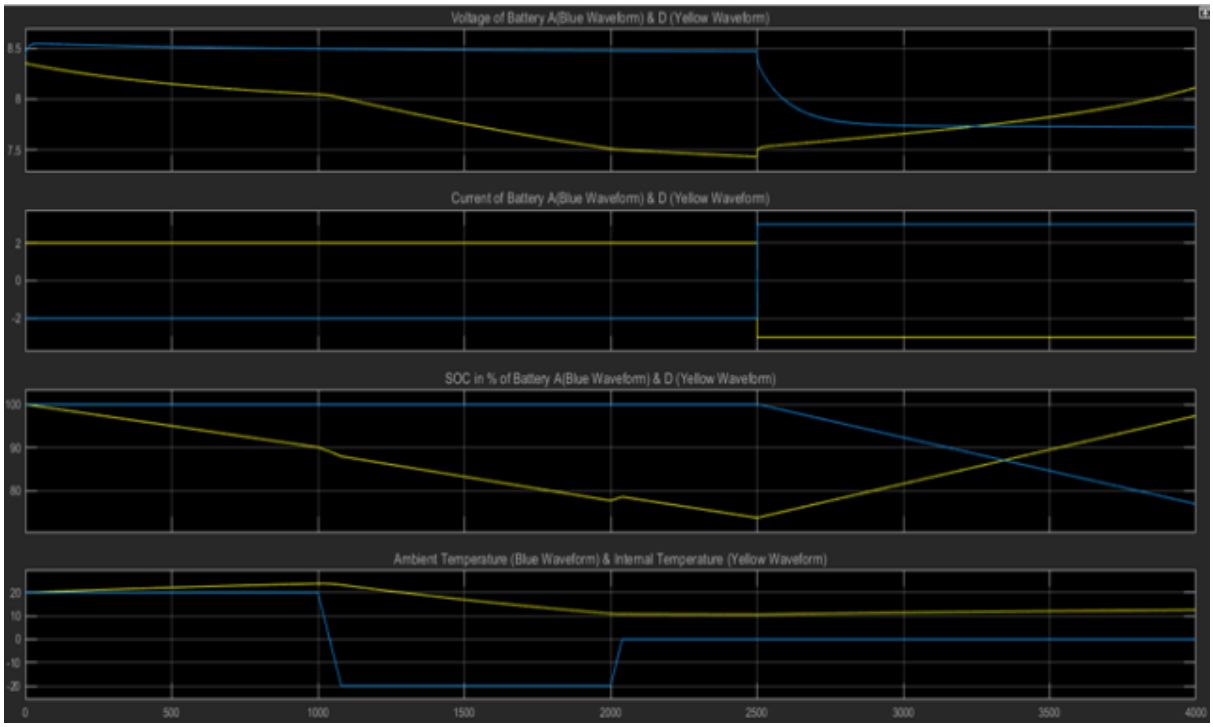

Figure 12. Effect of temperature on temperature-dependent charging and discharge characteristics of lithium-ion battery A & temperature-dependent nickel-cadmium battery D

4. Temperature Dependent Lithium-Ion Battery A & Independent Nickel-Metal-Hydride Battery E

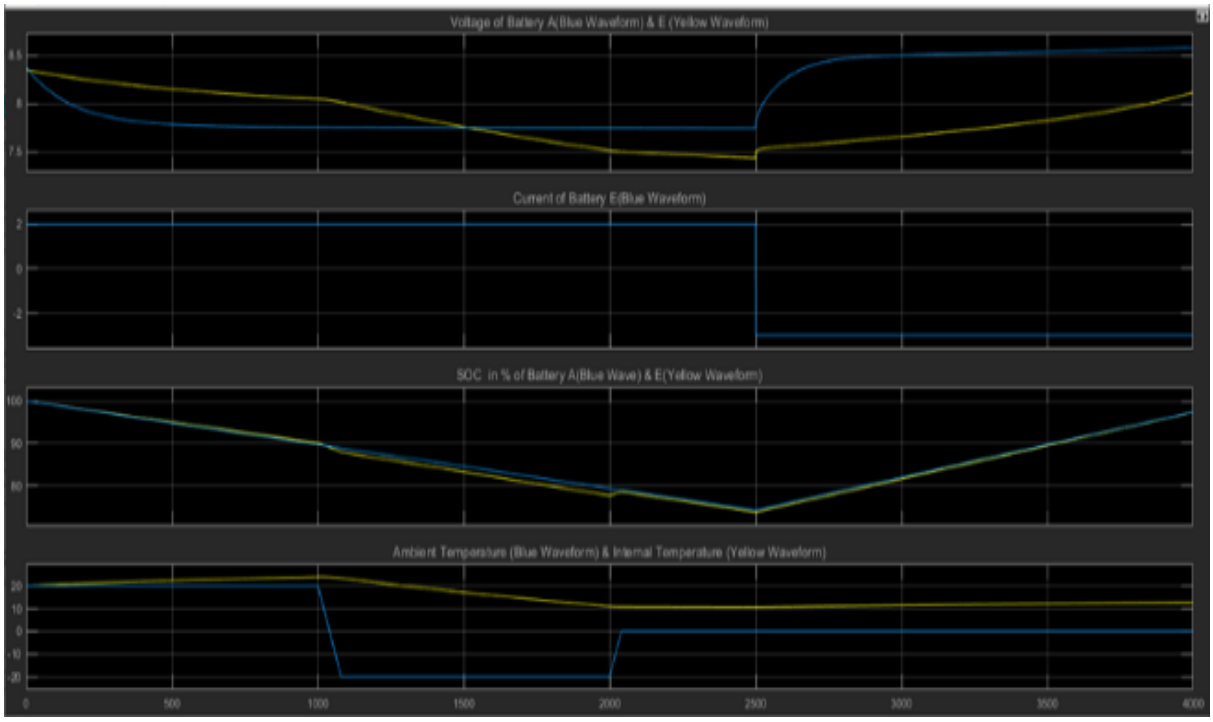

Figure 13. Effect of temperature on temperature-dependent lithium-ion batteries A & temperature-dependent charging and characteristics for discharging of nickel-metal-hydride batteries E.

5. Comparative Study of Temperature Dependent A & Temperature Independent Graphene Supercapacitor F Lithium-Ion Batteries

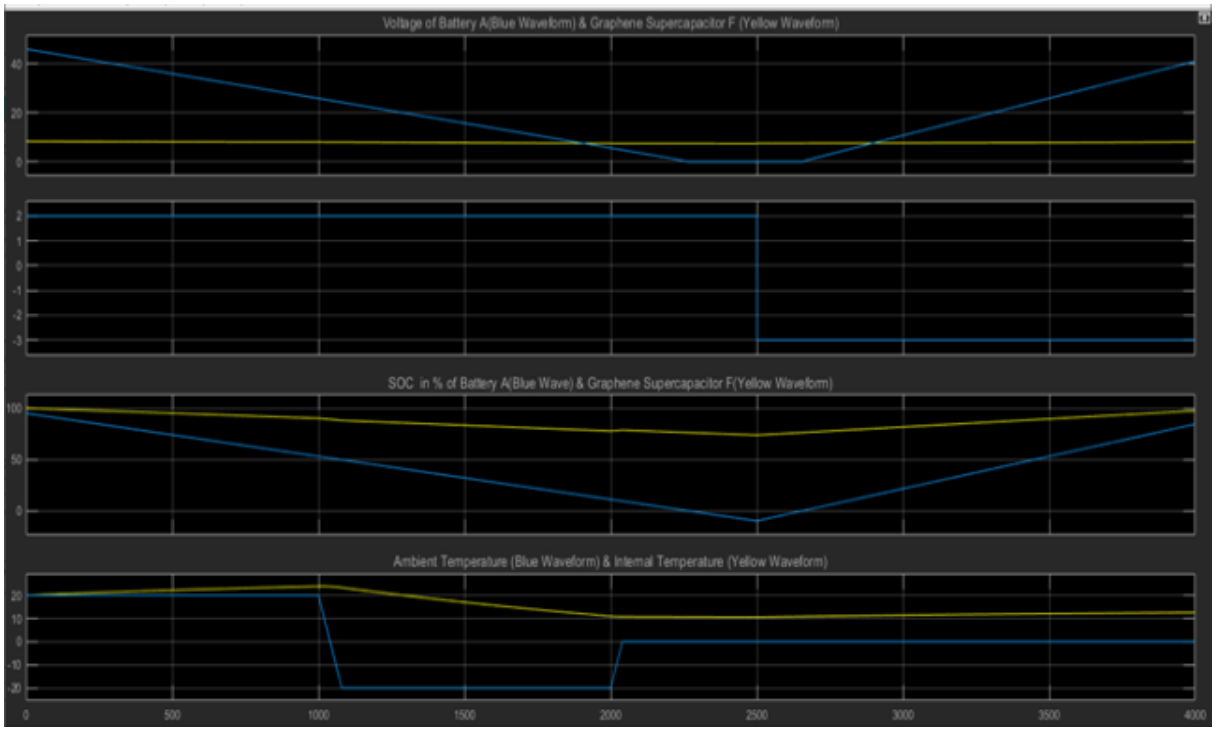

Figure 14. Effect of temperature on temperature-dependent lithium-ion batteries A and temperature-dependent charging and discharge characteristics of Graphene Supercapacitor F.

CONCLUSION

The combination of the benefits of quick charging and slow discharging is the greatest obstacle to the development of a modern energy storage system. Advanced studies suggest that graphene in storage devices can replace conventional devices in the future because it can charge and discharge up to 1,000 times faster than normal batteries. The exceptional graphene conductivity compared to diamond and copper allows the previous restriction to be overcome by the supercapacitor. In this research study, we built a model to analyze the behaviors of four conventional energy storage devices under MATLAB/Simulink® 2020a environment to analyze behaviors in different temperature conditions. In this research, temperature influence on efficiency, charging, discharging parameters such as Current, Voltage & State of Charge (SOC) when operating in 20°C and – 20°C temperature range detected and characterized under an analysis approach. In terms of change, we evaluated the results for temperature influence determination on battery charging and discharging parameters in comparison approach with graphene-supercapacitor after a deep observation of the above-mentioned waveform properties. This study may therefore play an important role in the creation of future perfect storage devices.

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