Research Article

Study Of Parametric Mismatch Of Supercapacitor Materials

Jaywant Suryawanshi [a], Alok Deep[b], R. S. Desai[c], P.B. Karandikar[d], R. M. Holmukhe[e]

[a]Research Scholar (M. Tech Electrical), Bharati Vidyapeeth (Deemed to be University) College of Engineering, Pune,
[b]Maharashtra, India, Research Scholar, Army Institute of Technology, Maharashtra, Indi
[c]Assistant Professor, Bharati Vidyapeeth (Deemed to be University) College of Engineering, Pune, Maharashtra, India.
[d]Associate Professor, Army Institute of Technology, Maharashtra, India
[e]Associate Professor, Bharati Vidyapeeth (Deemed to be University) College of Engineering, Pune.Maharashtra, India.
[a] jaywant.suryawanshi@gmail.com, [b]26alok2000@gmail.com, [c]rsdesai@bvucoep.edu.in, [d]pbkarandikar@gmail.com, [e] rmholmukhe@bvucoep.edu.in

Article History: Received: 11 January 2021; Revised: 12 February 2021; Accepted: 27 March 2021; Published online: 23 May 2021

Abstract: Since early 1980s, evolution in industrialization and rapid growth in population resulted in huge demands of automation and innovation in various sectors. One of the major innovations was energy storage systems. The present work is a research done on one of the modern-day energy storage devices i.e., Supercapacitor. Supercapacitor is an emerging energy storage device, and it has high potential to meet energy storage requirements for many applications in combination with batteries. Supercapacitors can be charged at faster rates and can deliver large output current. In this research, various components like electrodes, electrolytes, separators, and packaging materials are selected and tried to find the crux behind some of the issues in present day supercapacitor. This encapsulates various materials used in a supercapacitor, several parametric mismatches of the material used, and its impact upon capacitance value. This will help companies in manufacturing supercapacitors to select proper material having better characteristics.

Keywords: Supercapacitor, Electrodes, Electrolytes

1. Introduction

An energy storage device is an apparatus used for storing electrical energy when needed and releasing it when required. As a measure to counter global warming and other environmental degradation, the role of energy storage device technology in fields such as renewable energy generation and hybrid automobile systems will become important. When it comes to energy storage devices, Batteries have been the most prominent source in use till now. But batteries have their own limitations. Battery requires much longer time to charge, the output voltage supplied by batteries are quite low, it gives poor response to sudden power demand and use of batteries are mucky and grubby, when not operated with proper attention. One of the biggest pitfalls is its weight and makes it difficult in transportation and it is less portable. Hence, in the current scenario, supercapacitor is an operable replacement to batteries. Another reason which makes supercapacitor more inherent in use is rapid electrification of world. As world is moving towards using electric vehicles over current automobiles which run on conventional fuels like petrol, diesel; and in coming years engines will be replaced by motors that run on electricity. Hence it is important for nonstop modification and innovation in supercapacitor so that it becomes prominent energy storage device in various applications. In electrical circuitry, supercapacitors can be used as power boosters [1]. Supercapacitors also called Ultra-capacitors are electro-chemical storage device; whose capacitance value is much larger than conventional capacitors but displays lower voltage limits [2]. Supercapacitor in combinations or stacks can be a challenging power bank which can be used promisingly in automobile industry [3]. It typically stores 10-100 times more energy as compared with electrolytic capacitors, can accept and deliver charge much faster as compared to batteries. [4-6]. There are mainly two types of supercapacitors: Pseudo supercapacitor and double layer capacitor. It is seen that many papers have been published on supercapacitors related topic giving sufficient need and evidence about the urgency on further research on this topic [7-9]. Several electrode materials like Carbon Nanotubes (CNT), Mesoporous Carbons, and activated carbon like Vulcan, Vulcan XC72 R, etc have been tested with electrolytes. Similarly, several metal oxides have been tested with electrolytes such as potassium sulphate with manganese dioxide, sodium sulphate with manganese dioxide and lithium sulphate with manganese dioxide or ruthenium dioxide [10].

In supercapacitors, current collector is coated by porous carbon (electrolyte) and metal oxide. Biomass based materials can also be used as electrode in supercapacitors [11-12]. In this research paper various supercapacitors made from commercially activated carbon electrodes like VULCAN XC72 R, NORIT, PICA and NORIT are considered. The various electrolytes such as sulphuric acid, potassium sulphate, sodium sulphate and lithium sulphate are considered to study the performance and effectiveness of supercapacitor. The electrode-electrolyte double layer formed in the supercapacitor helps to store the charge[13-16]. On applying electric charge there occurs electrochemical reaction, these are the major reasons behind different charge storage capacity with different electrolytes [16-19]. Based upon relevant parameters above mentioned materials were analysed. With this purpose, this paper is structured into following sections. Section II describes materials in supercapacitor. Section III elaborates about selected parameters of supercapacitor material and its impact upon capacitance. Section IV gives concluding remarks.

2. Materials in SuperCapacitor

This section describes various materials used in the manufacture of supercapacitors.

A. Carbon Electrode Materials

Carbon materials are used as electrode material while manufacturing supercapacitor. It is due to its low cost, high selective surface area, availability, and electrode production technologies. These materials take part in double layer formations at the interface of electrode electrolyte as their storage mechanism. Hence, capacitance mainly depends upon the Specific Surface Area (SSA) available for electrolyte ions which is called as accessible SSA. Examples of the electrode forming carbon materials are: activated carbon, carbon aerogels, carbon nanotubes, graphene etc.

1. Activated Carbon

The most widely used are activated carbons for electrode of supercapacitors. They possess large surface area, lower cost, broader pores and good electrical properties. Activated carbon can be produced by physical and chemical process from carbonaceous substance. In this study VULCAN XC72 R, NORIT, PICA and YP50 has been considered for parametric mismatch evaluation. Fig 1 is the scanning electron microscope image of VULCAN XC72 R which shows good pore structure suitable for supercapacitor application.

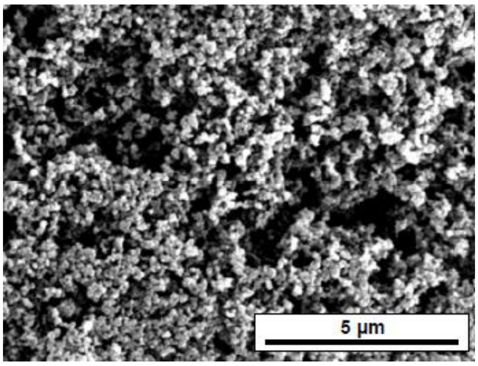

Fig. 1 SEM images of Vulcan XC72 R [22]

The SEM image of Vulcan XC72 R infers about its morphology, that the primary particle is aggregated and spherical in shape. Vulcan XC72 R has an intermediate structure between crystalline and amorphous called 'Turbostatic'. It consists of several crystal and graphene like layers with interplanar spacing of 0.35-0.38 nm which can be readily accessed by electrolytes [22],[23].

2. Carbon Nanotubes

With the continuous advancement of science, CNT is a significant innovation. Carbon Nanotubes are known for its distinctive pore structure, good thermal and mechanical stability, and superior electrical properties. CNT being mesoporous which allows continuous charge accumulation that utilize all the available surface area.

The small SSA of low-density CNT as compared with activated carbon can be chemically activated by adding potassium hydroxide. Which improves its specific capacitance.

3. Graphene

Graphene has grown its popularity in recent past. It consists of two-dimensional structure and is well known for its excellent traits of chemical stability, electrical conductivity, and large surface area. It is proposed to use graphene for electrode material because of its independence upon the pore distribution at solid states as compared with activated carbons and carbon nanotubes. Using graphene as electrode material has many other benefits. One of it is, it has major surface area as exterior which can be readily accessed by electrolytes. Different methods for producing different types of graphene can be of interests to many researchers. e. g, chemical vapor decomposition and micromechanical exfoliation methods.

B. Metal Oxides

Metal oxides are mixed with activated carbon to reduce internal resistance of the device. Metal oxides having high porosity are more suitable. Apart from this particle size, mass density and pore structure should match with activated carbon structure in order to select correct metal oxide. They show high specific capacitance and low resistance which makes them suitable for high energy density energy storage devices. The most popular in use metal oxides are manganese dioxide, ruthenium dioxide and Nickel oxide. Vanadium pentoxide and stannic oxides are also tried by researchers. In general, transition metal oxides are more suitable for supercapacitor construction. Follow subsections deals with some of the commonly used metal oxides in supercapacitor manufacturing.

1. Manganese Dioxide

Currently, manganese dioxide has been under spotlights for many researchers because of its good chemical and physical properties. It has large SSA. It is very cheap material and available in plenty. It is not only being cheap and environment friendly, but also has excellent capacitive performance in various electrolytes.

2. Ruthenium Dioxide

Both amorphous and crystalline nature of Ruthenium Dioxide makes it most suitable metal oxide in supercapacitor electrodes It has good characteristics like, high electrical conductivity, high electrochemical stability and excellent oxidation properties. It also has high thermal conductivity which makes its use feasible for supercapacitor applications. Ruthenium Dioxide received a great success in supercapacitor application, where the electrodes were found stable for more number of cycles. Only cost and its availability are the main issues with this metal oxide.

3. Nickel Oxide

One of the promising electrode materials is Nickel Oxide due to its environment friendliness, easy synthesis, and cheap manufacturing cost. Nickel hydroxide was transformed into Nickel Oxide resulting into higher specific capacitance. Nickel is available in plenty and has shown good results in some variants of lithium batteries. Thus, makes it good candidate for its use in supercapacitor electrodes.

C. Separators

Researchers are putting efforts to replace polyethene (PE) separators due to its adverse environmental impacts. Polythene being porous and non-decomposable material it becomes feasible for its application in supercapacitors. Ions of electrolyte passes through the PE separator easily and hence give better results in capacitance. SEM image of PE separator is shown in Fig 2 has porous and uniform structure which make them suitable for most of the electrical energy storage devices such as supercapacitor.

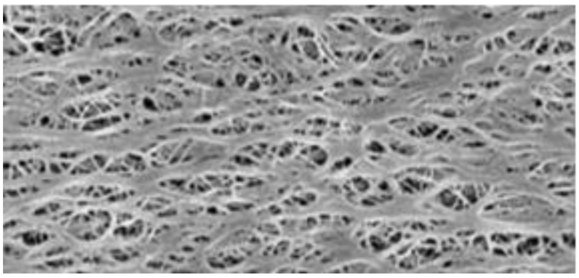

Fig. 2 SEM images of Polyethene separator [5]

Polyethene separator has branched structure which makes it porous and allows electrolyte particles to pass through it. Since polyethene is non decomposable and has poor thermal conductivity, it needs to be replaced by an alternate thermally conducting polymer which does not has any impact over environment degradation and is feasible in application of super conductor.

D. Current Collector

Current Collector (CC) is main part of electrode. It should have high thermal and electrical conductivity. If it is porous then it is more suitable. At present aluminum and stainless steels are used as current collector in foil form or wire mesh form.

E. Outer Packaging Material

1 Aluminium

Aluminium has excellent mechanical properties which makes it suitable for packaging of many products. It is lighter in weight, possess rigidity and toughness. It is noncorrosive. It forms a layer of aluminum oxide on its surface in the presence of oxygen which acts as good coating. For capacitor of any type, aluminium is most commonly used material in packing of the device.

2. Rubber

Polymers such as neoprene and isoprene are in great demand in automobile industries. However, rubber has excellent mechanical properties, noncorrosive, good insulator of current and due its cheap cost it is used in outer packaging of supercapacitor.

Parameters of Supercapacitor Materials

This section deals with some of the important parameters of the materials used in supercapacitors. In each subsection material parametric mismatch has been specifically pointed out. This will give clear direction to researchers for further studies. Identifying mismatch in the properties of materials used in supercapacitor is the main research contribution of the presented work in this paper.

A. Thermal Conductivity

Rate at which heat is transferred though the cross-section of the materials by means of conduction plays an important role in deciding the life of a supercapacitor. As a large amount of current is drawn from the capacitor, electrodes get heated. This heat should be transferred into the surrounding efficiently in order to use supercapacitor effectively over a longer run.

Materials used supercapacitor; their thermal conductivity is mentioned in Table I.

Table I. Approximate values of Thermal Conductivities(W/m*K) for generally used materials in supercapacitor.

Current Collector materials	Electrode materials	Separator materials	Packaging Materials
200-210	0.5-0.7.	0.2-0.5	0.09-0.63

It can be inferred from the Table 1 that thermal conductivity of electrode material and separator is much less than that of current collector. The value of thermal conductivity for all material used in supercapacitor should lie under same band or range for quick transfer of heat and preventing supercapacitor from getting damage. Further research is required on material engineering point of view. Separator with higher thermal conductivity is required. Various combinations e. g. electrodes in aqueous and non-aqueous electrolytes need to be experimented.

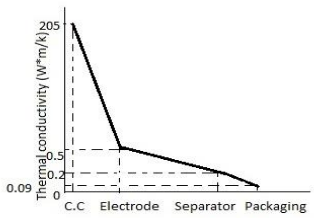

Fig. 3 Graphical representation of mismatch of thermal conductivity for generally used materials in supercapacitor.

It can be easily seen from Fig 3 that the thermal conductivity of supercapacitor material does not fall under same range. For high performance of super capacitor, the graph should ideally be a falling straight line. Line cannot be parallel to x axis as the intensity of heat transfer decreases when heat transfer progresses from one material to another.

B. Electrical Conductivty

Effectiveness of supercapacitor is primarily dependent upon the ability of the materials to conduct electric current. Electrodes, electrolytes, and current collector should have their electrical conductivity in same range. To improve electrical conductivity oxidizing agent like manganese dioxide and ruthenium dioxide is used depending upon the size of electrode particles and electrolyte. Materials used in supercapacitor and their respective electrical conductivity is mentioned in Table II.

Table II. Approximate values of Electrical Conductivity (mho/m) for generally used materials in supercapacitor

Current collector materials	Electrode materials		Separator materials	Electrolyte materials
	Manganese Dioxides	Carbons		
$36x10^6$ – $38x10^6$	0.006-0.02	50-53	10^{-13} -10^{-14}	5- 25

Electrical conductivity of separator is minimum as it is an insulating material. It is used to prevent short circuit between the two electrodes. From table II, it observed that electrical conductivity of electrolyte and manganese dioxide is very less and requires research in enhancing electrical conductivity of electrolyte. The use of composite electrodes wherein material with high electrical conductivity is preferred way of enhancing the performance of the supercapacitor.

C. Porosity

Volume of pores of material affects the specific surface area. Materials used in supercapacitor; their pore volume is mentioned in Table III.

Table III. Approximate values of Pore Volume (cucm/gm) for generally used material in supercapacitor

Current collector (Aluminium)	Electrode material		Separator (Polyethylene)	Electrolyte (K_2SO_4)
	MnO2	Carbon		
150-250	0.23	0.67	0.9-1.4	2.1-2.6

From the Table III, it is observed that the electrode material has lesser pore volume. At the smallest pore size, the surface area is functionally zero, however as the ions are too large to effectively enter the pores. Instead, when pores are too large, ions can easily access the pore surfaces, but the surface area is low. In order to improve performance of supercapacitor, sufficient space is required for accumulation of ions of electrolytes and hence further research is required in the field of materials suitable for application in supercapacitor with optimum pore volume.

D. Specific Surface Area

Not all pores are effective during charge accumulation. The most important properties of a material to describe type of material and physical significance upon adsorption and surface reaction are SSA. It is the property of solids defined as the total surface area by the mass of the material (m^2/g). Surface area available for adsorption of gases is an important factor for effective use of supercapacitor. While application of charges through electrodes, electrochemical reactions take place and gasses are evolved. Having high surface area in case of carbon results into high capability of accumulation of charges at the interface of electrode, electrolyte. Therefore, materials should have greater SSA [19-21]. Materials used in supercapacitor; their SSA is given in Table IV.

Table IV. Approximate values of the SSA (m2/g) of generally used materials in supercapacitor.

Electrode material		Separator (Polyethylene)
Manganese Dioxide	Carbon	
30-352	218-1336	0.013-16

VULCAN XC72 R has less SSA (213 m^2/g) as compared with other commercially available activated carbon such as NORIT (1000 m^2/g), PICA (1230 m^2/g) and YP50(1336 m^2/g). Therefore, for improving the characteristic of supercapacitor further research is required in the field of replacing Vulcan XC723 R or adding another material with higher SSA.

E. Particle Size

The size of particle and pore should be in the same range. The size of ions or molecules of electrolytes should be same as the pore size of electrode. Greater the surface match between ions and pores, more will be the capacitance. Materials used in supercapacitor, their particle and pore size are given in Table V.

Table V. Approximate values of the Particle Size (um) of generally used material in supercapacitor

Electrode materials	Separator	Electrolyte

Metal Oxide	VULCAN and PICA	NORIT and YP50	Materials	materials
0.057	0.02-0.05	50-250	50-60	0.03-0.2

From the Table V, it is noticed that commercially available activated carbons such as NORIT and YP50 has large particle size, but smaller pore size. For better performance of supercapacitor, electrolyte particles should completely get associated with electrode particle. Pore size of electrode should be equal to the particle size of electrolyte.

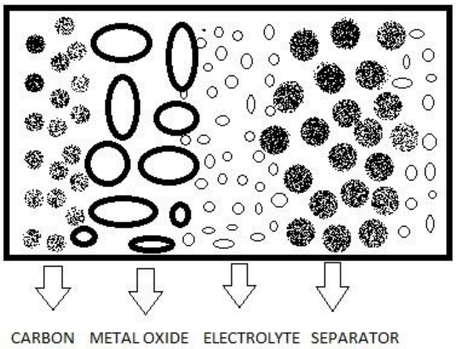

Fig. 4 Particle interface among current collector, electrode material, electrolyte, and separator in supercapacitor.

Fig. 4 show the particles of various materials used in supercapacitor. Particle size is different for various materials and hence structure made up of such materials is mechanically weak. The figure one shows the interface among materials of supercapacitor and its molecular arrangements. The electrolyte particles get associated on the surface of the electrode particle which is coated over stainless-steel mesh and a separator is placed in between the electrodes.

3. Conclusions

Supercapacitor is a very effective electric energy storage device which will play an important role in coming years for sectors like renewable energy, automobiles etc. The energy storage capability of a supercapacitor electrode is strongly influenced by particle and pore size, accessible surface area as well as porosity of the electrode material. Some other properties of electrode, electrolyte and other parts of the materials are required to be investigated collectively. Hence, relative studies of materials used in supercapacitor as a device was carried and presented in this paper. From this study some interesting facts came out in the form of conclusions. From the study, future expected course of action is also proposed. Following are the major outcomes the study carried out,

a) Thermal conductivity of materials used in supercapacitors does not facilitate the quick transfer of heat. It necessitates the experimentation on various new combinations of electrodes in aqueous and non-aqueous solutions to yield higher thermal conductivity. There is substantial variation in thermal conductivities of various materials used in supercapacitor. Separator forms bottleneck for heat transfer. Separator materials with better thermal conductivity need to be explored. Composite material as separator could be possible solution. Researchers need to work on this aspect.

b) The electrical conductivity of activated carbons may be improved by use of nano materials which will reduce the need of metal oxides. This will reduce the cost of the device which is major hurdle in its use in current situation. Electrical conductivity of electrolytes needs to be improved which can become good research area for scientist in chemistry domain.

c) The Pore size that optimises both surface area and pore accessibility is of importance. Specifically matching the pore size with the ion size is the key factor for maximising the capacitance.

d) As observed the SSA of available carbon electrodes needs to be further increased as that provides sites for formation of the double layer and hence boosts the capacitance. Activation of metal oxides to increase SSA needs to be investigated. Further, there is need to work on SSA of separator. If separator SSA is increased, then homogeneous interface between electrode material and separator material will be achieved which will make device compact and help in increasing specific capacitance. This will also result in more accessible surface area for ions to get stored.

e) As seen, there is wide difference in between the particle size of the electrodes such as activated carbon and electrolyte. It restricts adsorption in between the molecules of electrolyte and electrode. It is proposed to experiment with inexpensive and easy to obtain biomass based electrode materials prepared using physical and chemical activation to have better morphology that suits commercially available electrolytes.

It can be finally concluded that material aspects in supercapacitor needs to be considered collectively to avoid parametric mismatches. Approach of investigating materials for electrodes, electrolytes, separators etc. separately need to be changed.

Acknowledgment

The authors would like to acknowledge Dr. D.S. Bankar HOD Electrical engineering department BVDUCOEP for encouraging us to do research in pandemic situation..

References

1. B.E Conway,” Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications”, vol no-1, issue no- 1, pp. 2.
2. Martti Kaempgen , Candace K Chan, J Ma, Yi Cui and George Gruner . “Printable thin film supercapacitors using single-walled carbon nanotubes”. Nano Lett 2009 May ;9(5):1872-6.
3. Winter M, Brodd R,“What are batteries, fuel cells, and supercapacitors” J Chem Rev 2004, vol no-1, pp. - 201- 203
4. J. R. Miller and P. Simon. “Electrochemical Capacitors for Energy Management,” Science, vol.321, No.5889,2008, pp. 651-652.
5. Patrice Simon and Yury Gogotsi, “Materials for electrochemical capacitors.”, Nat Mater. 2008 Nov; vol no-7(11), pp. -400-404.
6. Chang Liu, Feng Li, Lai-Peng Ma and Hui-Meng Cheng, “Advanced materials for Energy Storage” Adv Mater 2010 Feb 23;22(8): E28-62, vol no-1; pp. 22.
7. P.B.Karandikar, D.B. Talange “Material Based Characterization of Aqueous Metal Oxide Based Supercapacitors”, IEEE International Conference on Power and Energy- kuala lumpur, Malaysia, Dec 2010, pp. 485-488.
8. Renjie Chen, H.-Q. Zhang, F. Wu, Bin Xu, Li Li and Snoopy Chen “Electrochemical Performance Matching Between LiTFSI/2- Oxazolidinone Complex Electrolyte and Various Carbon Materials with Different Pore Sizes and Surface Areas, Chemical Journal of Chinese Universities” -Chinese Edition-, April 2011, pp. 32(4):797-799.
9. Wei-Hong Jin, Gen-Ting Cao, Jing-Ya Sun, “Hybrid supercapacitor based on MnO2 and columned FeOOH using Li2SO4 electrolyte solution” Journal of Power Sources, January 2008, vol- 175(1), pp.686–691.
10. Laurence Athouël, Francois Moser, Romain Dugas, Olivier Crosnier, Daniel Belanger and Thierry Brousse, “Variation of the MnO2 Birnessite Structure upon Charge/Discharge in an Electrochemical Supercapacitor Electrode in Aqueous Na2SO4 Electrolyte”, The Journal of Physical Chemistry C 112(18),
11. S. Mathew, P. Kadam, M. Rai, P. B. Karandikar and N. R. Kulkarni, "Symmetric and asymmetric supercapacitors derived from banyan tree leaves and rose petals," 2016 IEEE Students' Conference on Electrical, Electronics and Computer Science (SCEECS), Bhopal, India, March 2016, pp. 1-4.
12. Frackowiak, V. Khomenko, K. Jurewicz, K. Lota and F. Béguin “Supercapacitors based on conducting polymers/nanotubes composites”. Volume no-153, issue no-2, pp.413-418.
13. M. Ishikawa, M. Ihara, M. Morita and Y. Matsuda, "Electric double layer capacitors with new gel electrolytes," Elecrrochlmica Acta, 1995, vol. 40, pp. 2217-2222.
14. Y. Matsuda, K. Inoue, H. Takeuchi and Y. Okuhama, "Gel polymer electrolytes for electric double layer capacitors," Solid State Ionics, 1998, vol. 113-115, pp. 103-107.
15. P. B. Karandikar, N R Kulkarni and Seema Mathew,. “Supercapacitors- Challenges Ahead,” Electrical India. November 2017, Vol 57, Issue 11, pp. 142-147.
16. Lewandowski and M. Krzyzanowski, "A new polymer electrolyte poly(acrylonitrile)-dimethylsulphoxide-salt for electrochemical capacitors", Electrochimica Acta, 2003, vol. 48, pp. 1325-1329.

17. P. B. Karandikar, Niraj Mahulkar and, Swati More, “New Trends in Supercapacitor.” IEEEMA Journal, May 2014, Vol 6, Issue 5, pp. 52-56.
18. Belhachemi, S. Rael and B. Davat, "A physical based model of power electric double-layer supercapacitors," Volume 5, pp. 3069-3076.
19. C. Arbizzani, M. Mastragostino, and F. Soavi, "New trends in electrochemical supercapacitors,",Nov 2001, Vol. 100, Issue 1-2, pp. 164 -170.
20. M. Nawa, T. N. And, and H. Mikawa, "Application of Activated Carbon Fiber Fabrics to Electrodes of Rechargeable Battery and Organic Electrolyte Capacitor ACCELERATED BRIEF COMMUNICATIONS," J. Electrochem. Soc., 1984, vol. 131, Issue 6, pp. 1457-1459.
21. C.M. Yang, J.B. Ju, J.K. Lee, W.I. Cho, B.W. Cho, "Electrochemical performances of electric double layer capacitor with UV-cured gel polymer electrolyte based on poly [(ethylene glycol) diacrylate]-poly (vinylidene fluoride) blend," Electrochimica Acta, 2005, vol. 50, pp. 1813-1819.
22. S. Mitra, A.K. Shukla and S. Sampath, "Electrochemical capacitors with plasticized gel-polymer electrolytes," Journal of Power Sources, 2001, vol. 101, pp. 213-218.
23. Seema Mathew, P.B.Karandikar and N.R.Kulkarni, “Modeling and Optimization of a Jackfruit Seed-Based Supercapacitor Electrode Using Machine Learning”. Chemical Engineering Technology, Vol. 43, Issue 9, September 2020, pp. 1765-1773..