Electrochemical behaviours of low-cost sustainable composite materials: Synthesis, application and optimization studies

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DOCTOR OF PHILOSOPHY

By

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Chapter 7

Conclusion and future studies

7.1 Conclusion:

In the present research, we synthesized different sustainable ternary composite materials for supercapacitor applications. Waste coconut-shell-derived activated carbon and binary metal oxides of XY_2O_4 type (where X, and Y are transition metals, and O is oxygen) were selected as supporting materials. PANI matrix was chosen due to its multiple redox states to enhance electrochemical performance; activated carbon was selected as it provides the low-cost porous scaffold, which helps in enhancing the power density, and binary metal oxides to enhance pseudocapacitance and energy density. Due to redox changes occurring at the electrode surface, transition metal oxides and conducting polymers have higher energy densities and specific capacitance. Metal oxides have poor cycle stability and low-rate capability due to their poor inherent conductivity. By providing enough surface area for the electroactive components (in this case, bimetallic oxides and polyaniline), activated carbon served the dual purposes of protecting the structural integrity of metal oxides and polyaniline and providing enough surface area to survive mechanical distortion during redox transitions. Different electrochemical parameters (such as specific capacitance, specific energy density, specific power density, capacitance retention, and charge transfer resistance) suggested that ternary composite materials performed better than pristine PANI matrix and its binary composite materials. Further, optimization studies of the ternary composite materials on the basis of weight percentage on specific capacitance was also conducted with the help of response surface methodology. Further, in this study, we have been able to achieve high specific capacitance and specific energy density and moderate power density. We also fabricated the electrodes with exceptionally low internal resistances. The capacitance retention still remains on the lower side and needs further work.

Polyaniline-activated carbon-copper cobaltite (PANI/AC/CuCo) exhibited a high specific capacitance of 613.5 Fg^{-1} at 1 mVs^{-1}. The symmetric device based on PANI/AC/CuCo demonstrated a high specific energy density of 44.1 Wh/kg and a maximum specific power density of 5997.1 W/kg. It also demonstrated excellent capacitance retention of 90.76 % of its initial value after 4000 cycles. A low charge transfer resistance of 5.6 Ω was obtained from the fabricated electrode. Further, the ternary composite material was optimized based on the weight percentage of its constituents towards the specific capacitance of the composite with the help of response surface methodology. The composite material with the proportion of 4:1:3 (polyaniline: activated carbon: copper cobaltite) showed an excellent specific capacitance of 694.8 F/g in a three-electrode configuration. The optimized ternary composite material demonstrated the highest specific energy density of 45.7 Wh/kg and specific power of 5998.7 W/kg. It offered a higher capacitance retention of 93.19 % after the completion of 4000 cycles. The obtained value of charge transfer resistance of the optimized ternary composite material PANI/AC/CuCo was 1.3 Ω.

Polyaniline-activated carbon-cobalt ferrite (PANI/AC/CoF) exhibited a high specific capacitance of 640.8 Fg^{-1} at 1 mVs^{-1}. The symmetric device based on PANI/AC/CoF demonstrated a high specific energy-density of 46.9 Wh/kg and a maximum specific power density of 6002.3 W/kg. It also demonstrated excellent capacitance retention of 84.56 % of its initial value after 5000 cycles. A low value of charge transfer resistance of 6.2 Ω was obtained from the fabricated electrode. Further, the ternary composite material was optimized on the basis of the weight percentage of its constituents towards the specific capacitance of the composite with the help of response surface methodology. The composite material with the proportion of 4:1.03:2.66 (polyaniline: activated carbon: cobalt ferrite) showed an excellent specific capacitance of 687.9 F/g in a three-electrode configuration. The optimized ternary composite material demonstrated the highest specific energy density of 47.5 Wh/kg and specific power of 6000.3 W/kg. It offered a higher capacitance retention of 76.1 % after the completion of 5000 cycles. The obtained value of charge transfer resistance of the optimized ternary composite material PANI/AC/CoF was 3.2 Ω.

Polyaniline-activated carbon-copper ferrite (PANI/AC/CuF) exhibited a high specific capacitance of 759.8 Fg^{-1} at 1 mVs^{-1}. The symmetric device based on PANI/AC/CuF demonstrated a high specific energy density of 49.6 Wh/kg and a maximum specific power density of 5996.6 W/kg. It also demonstrated excellent capacitance retention of 92.8 % of its initial value after 2500 cycles. A low charge transfer resistance of 5.3 Ω was obtained. Further, the ternary composite material was optimized on the basis of the weight percentage of its constituents towards the specific capacitance of the composite with the help of response surface methodology. The composite material with the proportion of 4:1:3 (polyaniline: activated carbon: copper ferrite) showed an excellent specific capacitance of 816.4 F/g in three-electrode configuration. The optimized ternary composite material demonstrated the highest specific energy density of 53.0 Wh/kg and specific power of 6000.1 W/kg. It offered a higher capacitance retention of 87.1 % after the completion of 2500 cycles. The obtained value of charge transfer resistance of the optimized ternary composite material PANI/AC/CuF was 4.8 Ω.

Out of all the three composite materials, the best result was shown by PANI/AC/CuF in terms of specific capacitance and specific energy density. This may be due to better growth of PANI on AC and CuF particles to create a better interconnected scaffold on these particles as suggested by sharp and distinct absorption bands of PANI (in composite) as evidenced by its FTIR spectrum. This interconnected scaffold covers and wraps the other components completely around to create more electroactive sites for the electrolyte ions and thereby outperforming other composite materials as a result of synergistic effects.

Activated carbon-based materials generally possess better power densities and cyclic stability at the cost of lower specific capacitance. Pseudocapacitive materials such as PANI and bimetallic oxides exhibit higher specific capacitance and energy densities due to the presence of fast reversible redox reactions involved. Therefore, combining activated carbon-based material with bimetallic oxides and polyaniline together provides adequate support and structural strength to withstand volumetric deformations of the overall composite material. However, it is not feasible to fabricate electrodes that exhibit all the positive effects, such as high specific capacitance, high power density, high energy density, and high cyclic stability from a single material. Therefore, the strategy of developing hybrid composite materials by including low-cost species using their advantageous characteristics and synergistic effects has shown promising results in the current study.

7.2 Future studies:

Future directions of the present work may include the development and performance optimization of electrolytes for the prepared composite materials. It is well known that no perfect electrolyte meets all the requirements and every electrolyte has its own advantages and disadvantages. The aqueous electrolytes (such as KOH used in the present study) offer high capacitance and conductivity but suffer from decomposition at high potential values. Organic electrolytes and ionic liquids offer higher working voltage windows, but their ionic conductivity is on the lower side. Further, electrolyte degradation, diagnosis, and mitigation studies could be performed addressing the failure-related phenomenon of the electrolytes. The proposed research direction would help in developing new-generation energy storage devices with superior electrochemical performance.

7.3 Feasibility analysis

The global supercapacitor market was valued at $1.5 billion in 2021 and is projected to grow at a compound annual growth rate of 30% from 2021 to 2030, potentially reaching $15 billion. This growth is primarily driven by the automotive and consumer electronics sectors, which currently account for 32% and 30% of the market share, respectively, with the energy sector following at 21%. Hybrid vehicles in automotive sector leverage the high power density and rapid charge/discharge capabilities of supercapacitors for acceleration, deceleration, and energy recovery during braking.

Supercapacitors have several significant disadvantages, including low energy density and a high rate of self-discharge. For instance, while a supercapacitor can lose half of its charge within a month, a lithium-ion battery typically only discharges about 5% over the same period. Additionally, the high initial costs and low energy density result in a higher cost per unit of energy stored ($/kWh) compared to other options like batteries. Despite these drawbacks, supercapacitors are well-suited for applications that require frequent, small bursts of energy, such as maintaining power quality or providing frequency regulation.

As EDLCs are the most mature of the three supercapacitor types as compared to pseudocapacitors and hybrid, most of the data available on performance metrics of supercapacitors belongs to EDLCs. Materials account for 71% of the manufacturing cost of an EDLC, with the active material being the most significant cost component within this percentage. The cost of activated carbon commercially available generally varies from USD 10-15. On the other hand, graphene and carbon nanotubes are other promising active materials. Graphene, which is a highly conductive material made from a single layer of graphite, enhances the electrode's surface area and thereby increases its capacitance. It has been reported that use of graphene increases the energy density by 72%. Manufacturing of graphene on a large scale is a major challenge currently being explored by both the lithium-ion battery and supercapacitor industries. Significant improvements and innovations are required to get the manufacturing cost of graphene reduced in order to be competitive with activated carbon.

Further, it has been established that with the use of pseudocapacitive materials like (conducting polymers and metal oxides), higher specific capacitance can be achieved as the density of the redox sites on the electrode surface can be significantly larger than the density of the ions absorbed in a traditional EDLC. As a consequence, these materials are able to store 10-100 times more specific energy than a pure EDLC. The challenges with these materials include the swelling and contraction of the resulting pseudocapacitors (PCs) during charging and discharging, which can lead to degradation, safety concerns, and reduced cycle life. The same statement also holds true for composite materials (binary or ternary) where increasing the energy density leads to a reduction in cycle life. Finally, an attempt has been made to present the performance metrics normalized to the cost of materials used in this work. For comparison, the material costs for a 2.7 V, 3500 F EDLC supercapacitor, 4.5 Wh/kg, 1000 W/kg (95 eff.) and a battery (100 Wh/kg, 1000 W/kg) has been used for reference based on literature available.

Table. 7.1: Cost comparison for feasibility of synthesized ternary composite materials in this work (All costs in USD)

Material	specific capacitance	Energy density Wh/kg	Power density	Cost/energy density	Cost/power density
PANI/AC/CuCo*	694.8	45.7^	5998.7^	1.6^	1.78
PANI/AC/CoF*	687.9	47.5^	6000.3^	1.8	2.04
PANI/AC/CuF*	816.4	49.6^	5996^	0.55	0.85
EDLC capacitor	-	4-10	1000-3000	1-6	0.5-2.5
Battery	-	25-450	150-2250	0.3	2.55

(*cost of materials Includes 50% extra cost as assumption for processing cost)

(^ based on mass of electroactive material)

It is very clear from the above table that EDLCs (and hybrid supercapacitors) cannot compete with batteries in terms of cost/energy density but they can compete in terms of cost/power density and cost / unit. Both energy storage technologies must provide same power and cycle life and sufficient energy for application. Further, the ternary composite materials synthesized in this work also seem to be cost competitive (Table. 7.1) after preliminary assessments in terms of cost/energy density as compared to that of the commercial EDLCs.

7.3 Commercial and techno-economic aspects:

The ternary composites for supercapacitors, which usually consist of three distinct materials combined, have garnered a lot of attention since they have the potential to improve energy storage devices' performance. The important considerations in their commercialization have been discussed below:

Supercapacitors, with their distinctive capabilities, are leading advancements in consumer electronics and automotive transportation. In the automotive industry, they are mainly employed for power delivery and energy recovery, particularly through the capture of braking energy. They are also utilized to supply backup power in consumer electronics like GSM/GPRS communication devices, thermal printers, LED flashlights, GPS chips, and barcode scanners. When integrated into hybrid systems with batteries, supercapacitors can extend battery life by (i) delivering power as needed and (ii) minimizing voltage drop strain. To some extent, supercapacitors can serve as an intermediary between traditional capacitors and lithium-ion batteries.

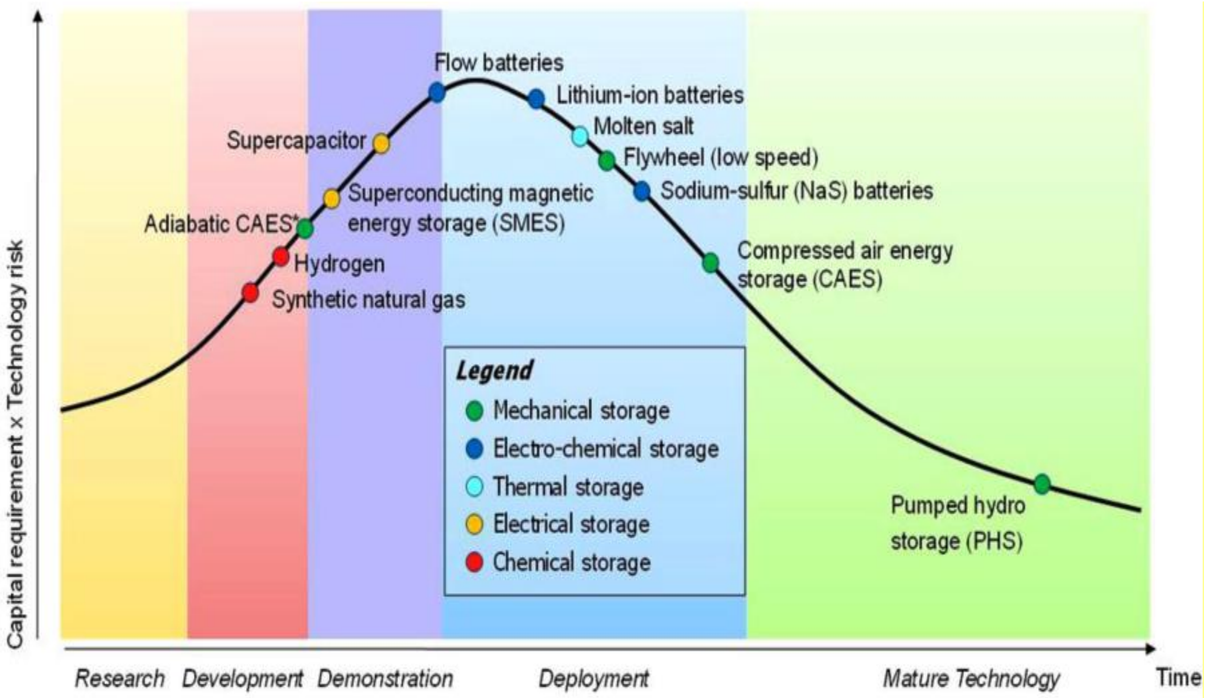

Fig. 7.1: Techno-commercial maturity of various energy storage systems (Source: Schlumberger Business Consulting (SBC) Energy Institute, [265])

Fig. 7.1 provides an insight into the techno-commercial maturity standard of several energy storage systems. The horizontal axis represents the various stages of technological development, ranging from the research phase to a fully mature technology. The vertical axis reflects the multiplication of capital requirements and the technological risk associated with each system. The techno-commercial maturity plot offers a quick overview of where research focus should be directed, highlighting areas that need detailed design work and cost estimation in comparison to other storage technologies.

Supercapacitors are located in the purple zone of the plot, known as the demonstration zone. This indicates that while supercapacitors have made significant progress, they have not yet achieved full technological maturity. However, with continued research and development, supercapacitors have the potential to reach a broader commercial market. Despite ongoing research and interest, supercapacitors are far from achieving the standard required to replace batteries or becoming a leading energy storage technology. The number of research labs and companies focused on supercapacitor production remains relatively low from Indian point of view.

Further, the energy storage system (ESS) market in India is still in its early stages but offers significant opportunities with considerable growth potential. Recently, several initiatives have been implemented to promote the expansion of distributed ESS in the country. Indian Energy Storage Alliance (IESA) in its recent study has projected the renewable energy integration of upto 61 % by the year 2030 [264].

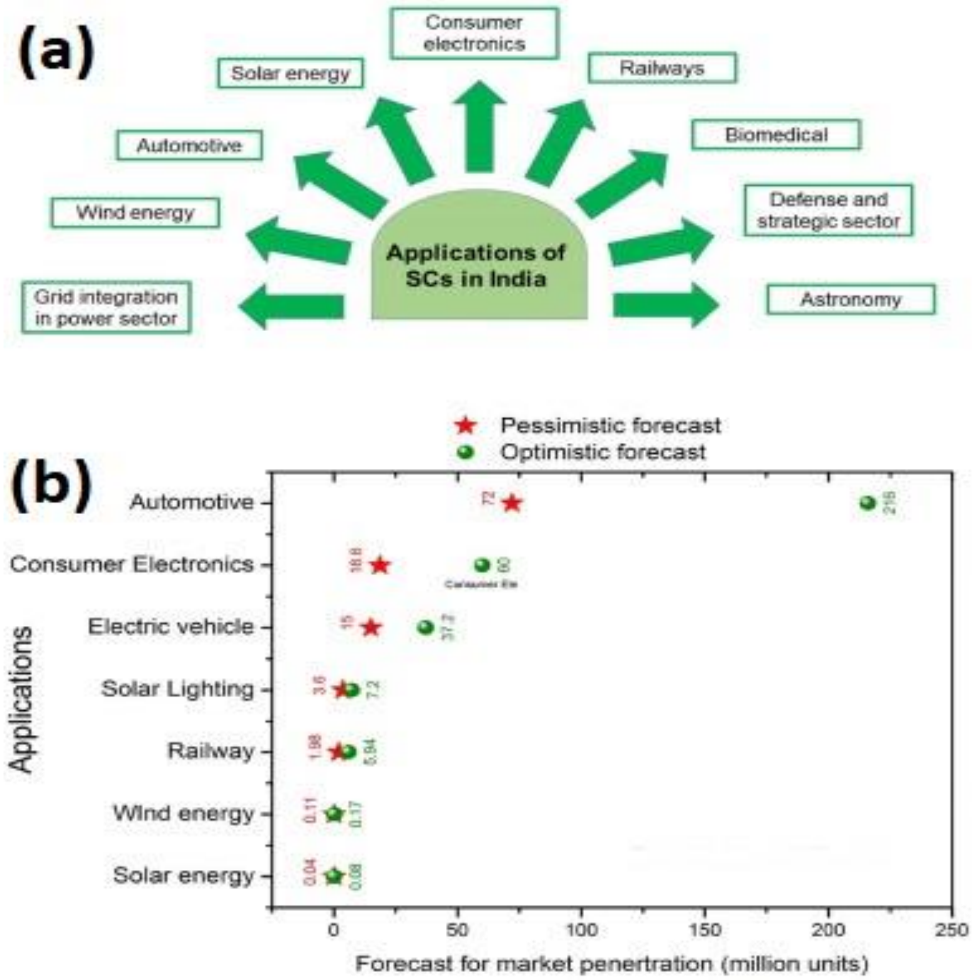

Fig. 7.2: (a) Applications of Supercapacitors (SCs) in India. (b) Optimistic and pessimistic forecast for market penetration of supercapacitors in India. (Electronics Industries Association of India, ELCINA) [265].

The applications of supercapacitor devices and their optimistic/pessimistic forecast for market penetration of supercapacitors in India has been presented in Fig. 7.2 (a) and (b).

Over the past decade, India's supercapacitor market has experienced steady growth. In the 2013 fiscal year, the market was valued at $10.7 million. At that time, the U.S. accounted for 43% of the global market revenue, followed by Europe at 26% in 2014, while India's share was less than 3%. However, the Indian supercapacitor market grew at a compound annual growth rate (CAGR) of 16% from 2017 to 2022. Key factors driving this growth include (i) increasing demand for consumer electronics, (ii) the expanding electric vehicle market, and (iii) greater emphasis on the solar and wind energy sectors. Consumer electronics applications encompass laptops, smartphones, TVs, GPS devices, cameras, and more. Finally around ~42% of the overall electric supply is supposed to come from electrochemical energy storage, provided India fulfills its potential to become a country with 100% renewable energy sources by the year 2050 [265].

7.4 Cost comparison of supercapacitor materials:

When comparing the cost of supercapacitor materials, it's important to consider both the raw material costs and the processing costs associated with each material. Supercapacitors, also known as ultracapacitors, store energy through electrostatic charge rather than chemical reactions, and their performance heavily depends on the materials used for electrodes, electrolytes, and separators.

An overview of comparison of cost and type of supercapacitor materials based on electrochemical properties available in literature has been presented in Table. 7.2 below.

Table. 7.2: Comparison of cost and type of supercapacitor materials based on electrochemical properties

Technology ype	Electrode aterials	Energy storage mechanism	Approximate Cost	Specific Capacitance (F/g)	Cell-voltages (V)	Energy density (Wh/kg)	Power density (kW/kg)
EDLC	Activated carbon	Charge separation	Low	50-250	2.5-3	4-10	1-3
Advanced carbon	Graphite carbon	Charge transfer or intercalation	Moderate	200-500	3-3.5	8-12	1-2
Advanced carbon	Nanotube forest	Charge separation	Moderate-high	300-700	2.5-3	Not known	Not known
Pseudocapacitive	Metal odixe/conducting polymers	Redox charge transfer	High	200-2000	2-3.5	10-15	1-2
Hybrid	Carbon/metal oxide/conducting polymer	Charge separation/ redox charge transfer	Moderate	200-1500	1.5-3.3	10-15	1-2

Composite Materials (This work*)	Carbon/metal oxide/conducting polymer	Charge separation/ redox charge transfer	Moderate	694.8-816.4	1.2	45.7-49.6	5996-6000.3

*Based on mass of electroactive materials

Although supercapacitors have existed for over 50 years and are commonly used in various applications, their potential in power systems has not been fully realized. This is primarily due to three factors: their low energy density, high costs, and limited awareness of their advantages. For, further improvenets in cost and performance of composite materials, several measures may be taken which are discussed as follows:

(i) For increasing the energy density, various cost reduction methods may be followed to purify and process the carbon materials.

(ii) New design and innovations is also required in the development of composite materials so that cycle life, energy density and power density can be tailored for specific end use applications.

(iii) Research and development studies should also be carried out in search of better electrolytes, separators, current collectors in order to increase the specific energy and specific power for next-generation applications.

(iii) The problem of high self discharge in case of supercapacitors should also be addressed in order to make this technology more feasible and increase its shelf life thereby reducing overall life cycle costs.

(iv) Finally, awareness should also be increased for analysis of various other uses of suparcapacitors including potential hybridized energy storage technologies with respect to the combined cost and performance relative to the requirements.