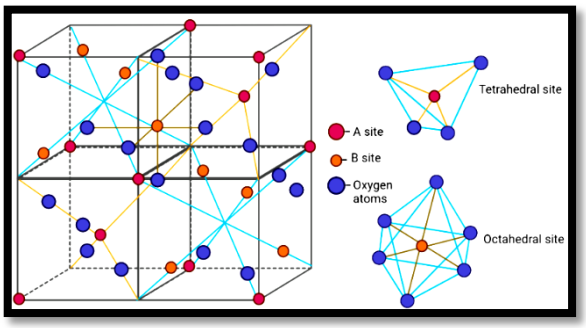
SPINEL MAGNETIC COBALTITES FOR THE APPLICATIONS AS SUPERCAPACITORS

Abstract

Transition metal oxides (TMOs) have gained enormous heed in the last decades with their ability to deliver high capacitance. Importunity of futuristic, economical, and eco-friendly energy storage devices with more power/energy densities have increased outstanding interest in inventing new materials that boost performance to fulfill the energy requirements of modern society. Spinel Cobaltite (AB_2O_4), A, and B for tetrahedral and octahedral configurations of oxygen to form a closed packing of the cubic lattice.



Spinel Structure of Cobaltites

The physical and chemical properties of cobaltites depend upon their chemical composition and microstructural characteristics, which further depend on the synthesis methods with which they have been synthesized. The methods often include sol-gel, hydrothermal, electrospinning, and chemical processes. The different cobaltites with different chemical compositions are Co_3O_4[Tricobalt tetra oxide(CCO)], $FeCo_2O_4$[Iron cobaltite(FCO)], $CuCo_2O_4$[Copper cobaltite(CuCO)], $NiCo_2O_4$[Nickel cobaltite(NCO)], and $ZnCo_2O_4$[Zinc Cobaltite(ZCO)]. The Iron Cobaltite was found to exhibit ferromagnetic behavior at room temperature. The Co_3O_4 nanorods exhibit ultra capacitance of 281 Fg^{-1}. The $FeCo_2O_4$ microspheres,

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nanosheets, nanoflakes, and nanofibers, exhibit ultra capacitance of 231.5 Fg^{-1}, 339 Fg^{-1}, 433 Fg^{-1}, 165 Fg^{-1} respectively. Also, the $ZnCo_2O_4$ nanowires show a value of about 1400 Fg^{-1}. The nickel cobaltite nanosheets and Copper cobaltite show the most prominent supercapacitive behavior having values of 2282 Fg^{-1} and 3080 Fg^{-1}.

Keywords: Cobaltites, Supercapacitance, Spinel, Energy storage.

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I. INTRODUCTION

Supercapacitors (SCs) are renewable energy storage devices that assist in traversing the space between conventional capacitors and batteries. SCs acquired enough attention due to their unique characteristics like eco-friendly, long-term stability, and high-power density. The praise for capacitor technology's genesis goes to the Leyden Jar's creation (1745-1746), which was fabricated using glass vessels with metal foils. During charging, the positive charges are gathered on one electrode and negative on the other. A discharge process would occur by connecting these two charges with a metal wire. As a rule, Supercapacitors are comprised of an electrolyte, the negative electrode, and an interelectrode called separator. In this respective electrode solution, the electronic conductivity of the electrode and ionic conductivity of the electrolyte would take place, by which a double electric layer will form on the solid-liquid interface. The internal resistance on the surface of the junction between the electrode and electrolyte and heat generated by this internal resistance starts collected near the electrode, which puts further higher requirements for the thermal diffusion of the electrode [1].

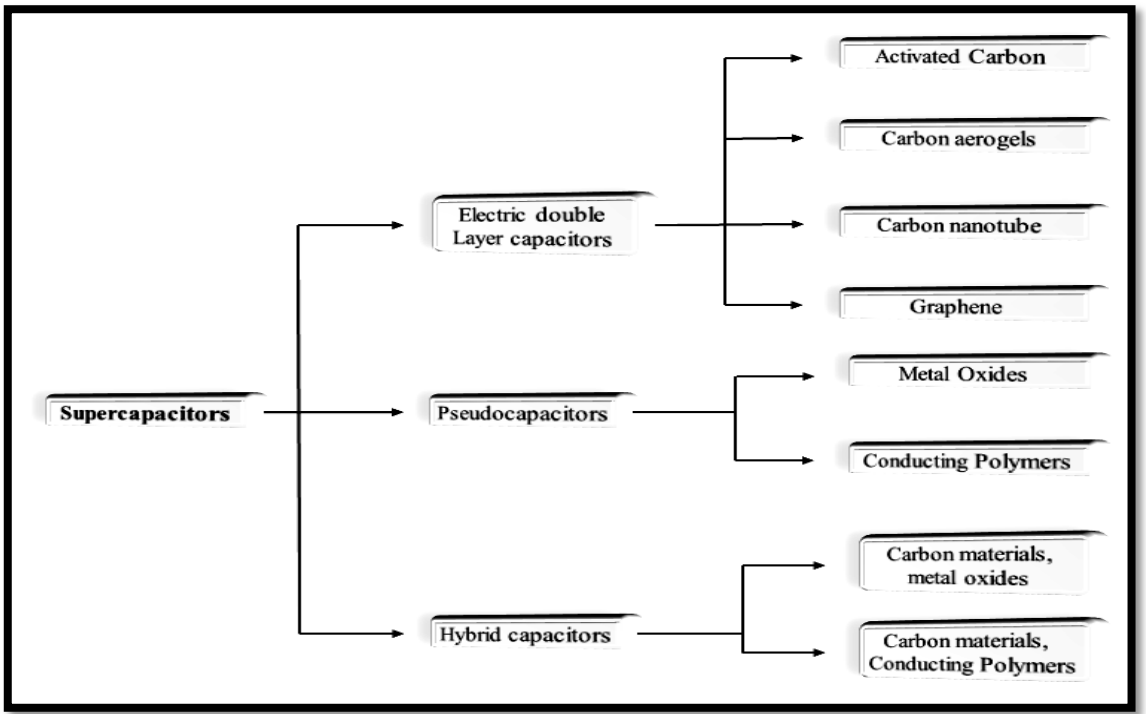

Figure 1: Flowchart of classification of Supercapacitors

The materials having a large surface area have more tendency to transfer the charges on the surface, called pseudo capacitive behavior, having more capacitance. On the other hand, when the charge stored between the interface of electrode and electrolyte is called electric double-layer capacitance has superior cyclic stability and higher reversibility but lower capacitance [2]. The generation of heat should be avoided by reducing the ripple current during the charging and discharging process. Supercapacitors are categorized into three types: (1) Electric double-layer capacitors (EDLC), (2) Pseudocapacitors, and (3) Hybrid capacitors, as shown in Fig.1.

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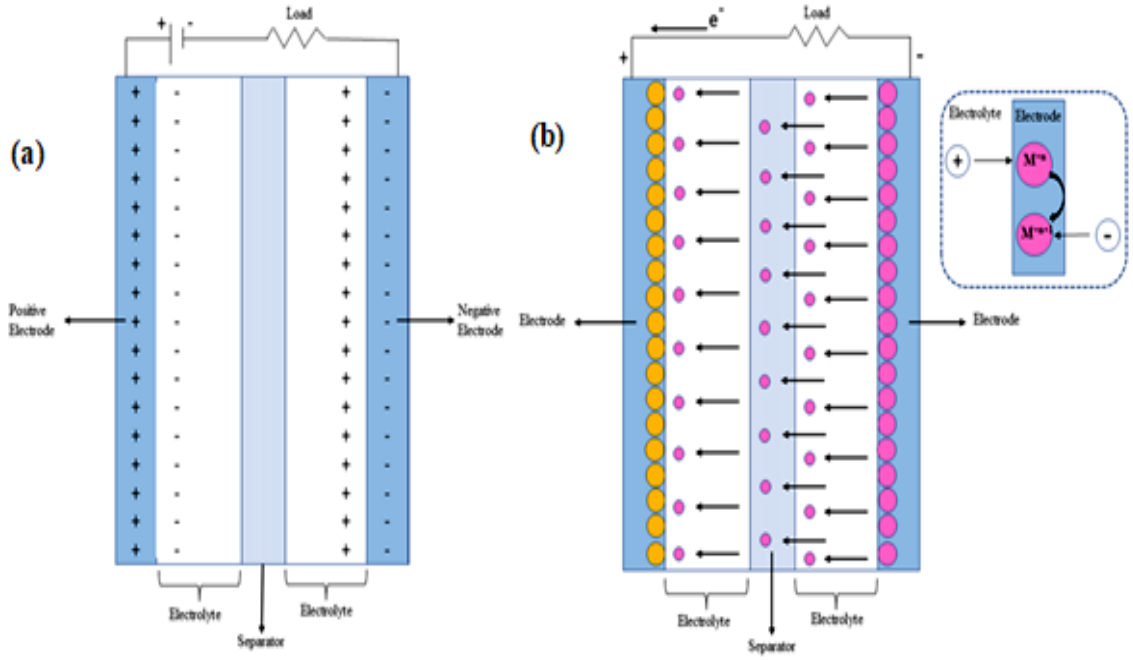
II. BASICS OF SUPERCAPACITORS

In EDLCs, electrostatically charged storage takes place, known as non-Faradaic. The energy storage mechanism based on the separation at the electrochemical interface formed between the electrolyte and electrode layers results in no shifting of charges between them. This outcome constructs them as highly reversible along with high cyclic stability. Carbon-based materials, for instance, activated carbons (ACs), carbon nanotubes (CNTs), carbon aerogels, graphene, etc., are extraordinary compositions for EDLC with gigantic specific surface areas with excellent electrical conductivity and mechanical and chemical stability. In distinction, pseudocapacitors are involved with the faradaic charge transfer process by which pseudocapacitance depends on the chemical affinity of the materials of the ions absorbed on the surface of the electrodes. These absorbed ions don't react with the material, so the transfer of charges occurs only. This faradaic procedure would approve pseudocapacitors to attain high specific capacitance and energy density. Materials that evident faradaic behavior and are suitable for pseudo capacitor are conducting polymers, e.g., polypyrrole (PPy), polyvinyl alcohol (PVA), polyacetylene, polyaniline, polythiophene, etc., transition-metal oxides (TMOs), e.g., RuO_2, Fe_3O_4, V_2O_5, MnO_2, Co_3O_4, IrO_2, etc. On a note, pseudocapacitors usually come up with higher energy density at the cost of shorter life cycles and lower rates in comparison with EDLCs. Hybrid capacitors were firstly explored in 2007 has both EDLCs and pseudocapacitors characteristics. The charge storage mechanism is followed by both Faradaic and non-Faradaic processes [3]. In this capacitor, a carbon electrode gets combined with a Li-ion electrode that enhances the capacitance by decreasing the anode potential with an increase in cell voltage, which results in the enhancement of energy density.



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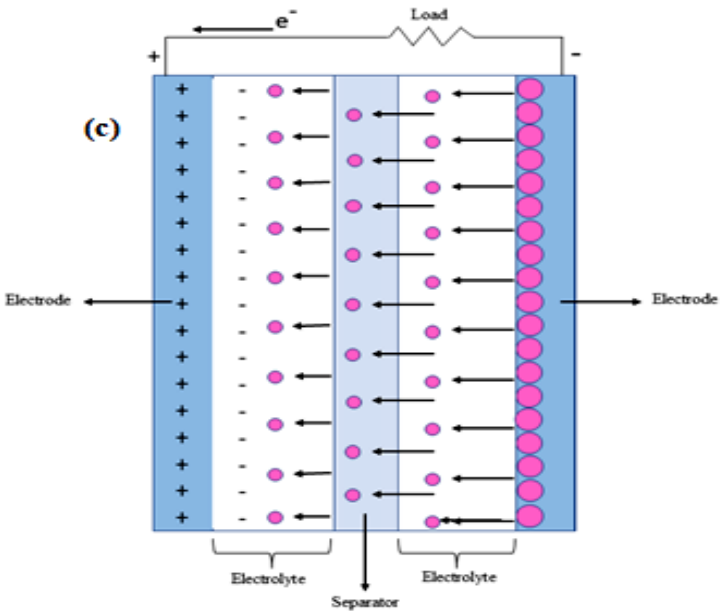

Figure 2: Schematic Depiction of types of Supercapacitance (a) EDLC (b) Pseudocapacitor (c) Hybrid Capacitor

Supercapacitors are commanded by the same fundamental equation that is used for traditional capacitors by which capacitance gets calculated from the conventional capacitance. Given capacitance,

$$\mathbf{C = \varepsilon_o \varepsilon_r A_e / d}$$

On the other hand, the specific capacitance by cyclic voltammetry is calculated from the equation,

$$\mathbf{C = I\, \Delta t / \Delta v}$$

Where *C*, *I*, *t*, and Δ *V* are the SC (Fg^{-1}) of the electrodes [4].

III. TRANSITION METAL COBALTITES

Transition metal oxides (TMOs) have gained enormous heed in the last decades with their ability to deliver high capacitance. The importunity of futuristic, economical, and eco-friendly energy storage devices with more power/energy densities have increased outstanding interest in inventing new materials that boost performance to fulfill the energy requirements of modern society. By periodic table, cobalt belongs to the first transition metal series with electronic configuration [Ar] $4s^2$ $3d^7$. Like transition metal ferrites, with the general formula AB_2O_4, the B-position is always occupied by Iron (Fe), and A-position gets substituted by various transition metal elements like nickel, Zinc, copper, manganese, etc. to get nickel ferrite ($NiFe_2O_4$), Zinc ferrite ($ZnFe_2O_4$), Copper ferrite ($CuFe_2O_4$), Manganese ferrite ($MnFe_2O_4$) respectively accordance with the properties and applications. Thus, they are called transition metal ferrites. Similarly, in the case of cobaltites, the B-position is always occupied by cobalt (Co), and A-position gets substituted by various transition metal elements for desired properties and applications. Thus, they are known as transition metal cobaltites.

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Transition metal cobaltites (TMCs) have excellent properties of electrochemical performance, such as low internal resistances and fast electron transfer ability due to numerous oxidation states and complex structures, which results in higher stabilities. Due to the unique spinel structures of TMCs, having a massive number of active centers and ion diffusion sites by which electrons are transferred swiftly gives high theoretical specific capacities [5]. Therefore, TMCs have excellent applications as electrode materials. In general, the formula for spinel magnetic cobaltites is AB_2O_4, where A and B indicate the tetrahedral and octahedral configurations of oxygen atoms to form a closed packing of the cubic lattice.

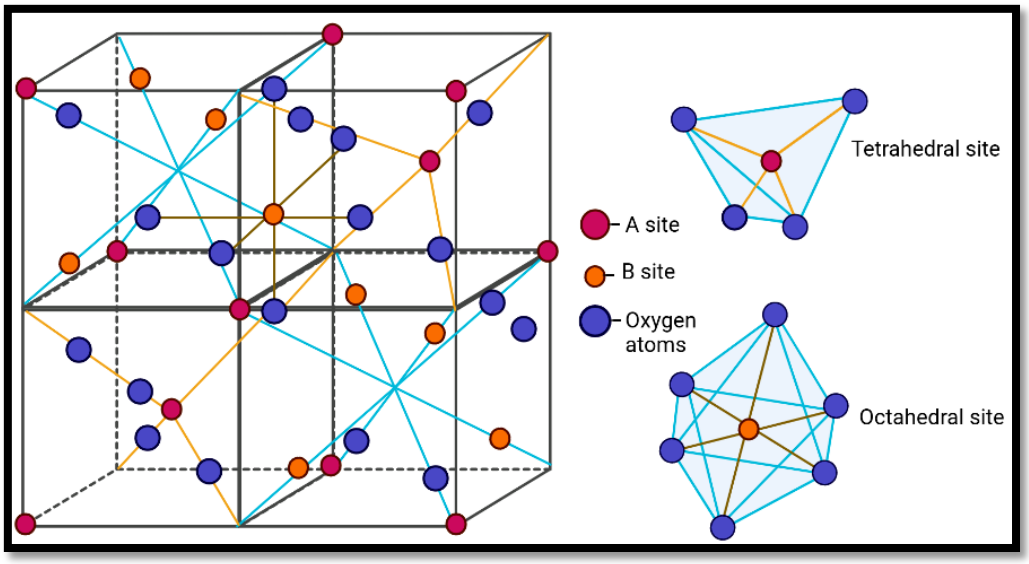

Figure 3: Schematic Depiction of Spinel Structure

In standard, carbon/carbon oxide-based materials are used in EDLC because charges get stored electrostatically. On the other side, transition metal oxides (TMOs) are used for pseudocapacitors because charges get transferred on the surface by faradaic redox reactions to generate high capacitances. The physical and chemical properties of spinel cobaltites depend on their chemical composition and microstructural characteristics, which further depend on the synthesis methods with which they have been synthesized. TMCs have been synthesized into nanomaterials with various morphologies like nanosheets, microspheres, nanofibers, nanoflakes, nanorods, nanopowders, etc. These different morphologies with high specific surface area and great electrical conductivity consequences in outstanding electrochemical performance. The different cobaltite with different compositions are Co_3O_4[Tricobalt tetraoxide(CCO)], $FeCo_2O_4$ [Iron cobaltite(FCO)],, $CuCo_2O_4$ [Copper cobaltite(CuCO)], $NiCo_2O_4$ [Nickel cobaltite(NCO)], and $ZnCo_2O_4$ [Zinc Cobaltite(ZCO)].

1. **Spinel Magnetic nanoporous Co_3O_4 (CCO) nanorods:** The nanoporous Co_3O_4 nanorods were synthesized using the hydrothermal method via the sintering route. The M-H (Magnetisation vs. magnetic field) magnetic characterization by VSM (Vibrating sample magnetometer) reveals the antiferromagnetic behavior of CCO at 5 Kelvin, 100 Kelvin, and 200 Kelvin with a field of 7 Tesla as shown in Fig.4 [6].

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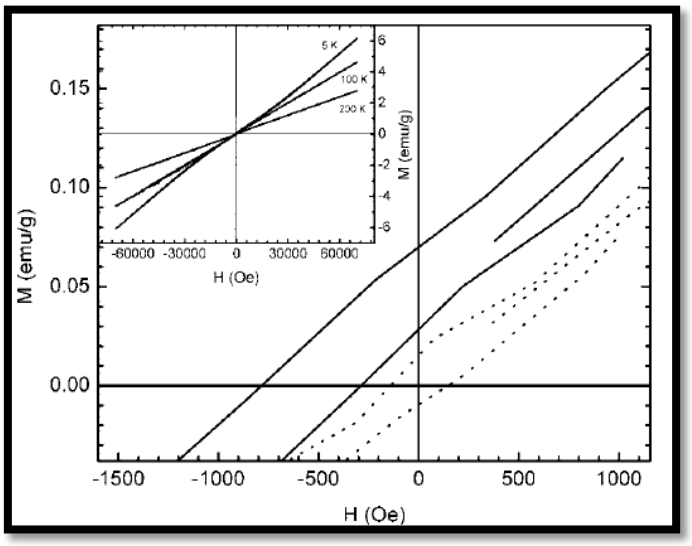

Figure 4: The M-H graphs (Magnetization vs. magnetic field) of CCO at 5K, 100K, and 200K [6]

The Transmission electron microscopy (TEM) at low magnification around two microns image shows the successful fabrication of nanorods at the resolution of 2 micron in Fig.5.

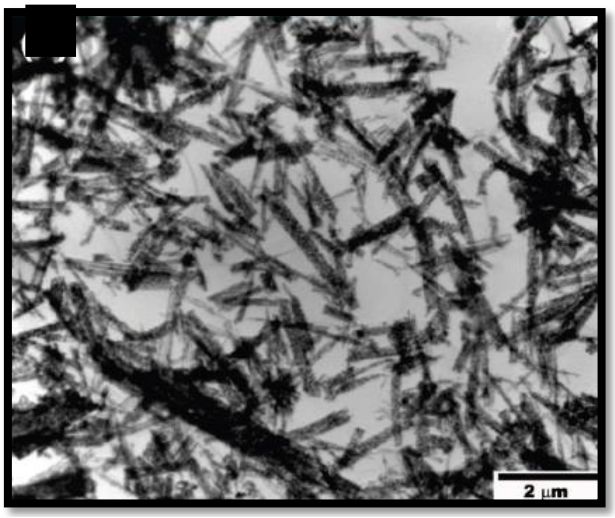

Figure 5: Low magnification TEM image of Co_3O_4 nanorods [6]

Three electrode system was used for testing the super capacitance in which PVDF (polyvinylidene difluoride) and carbon black took as the working electrode. The platinum foil and saturated calomel electrodes were used as counter and reference electrodes. The value of capacitance was reported as $281Fg^{-1}$ for CCO nanorods in Fig.6 [6].

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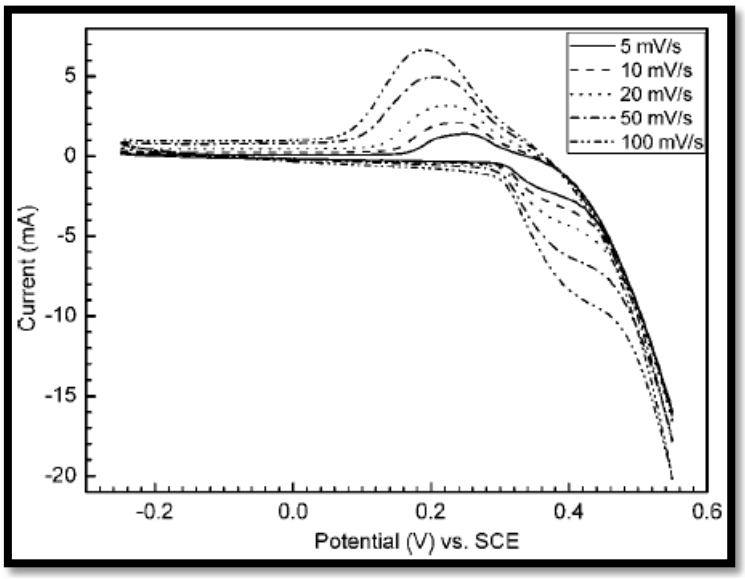

Figure 6: Cyclic voltammetry curves of CCO nanorods [6].

2. **$FeCo_2O_4$ nanofibers:** The FCO nanofibers were prepared by the electrospinning technique. The electrospinning technique is basically used for the fabrication of nanofibers of desired materials. The Fourier transform scanning electron microscopy (FESEM) image reveals the proper fabrication of FCO nanofibers. Also, the M-H loop of FCO nanofibers obtained from SQUID (Superconducting quantum interference device) at room temperature declares the ferromagnetic nature in Fig.7. The CV graphs show the specific capacitance value of 165 Fg^{-1} in Fig.8 [7].

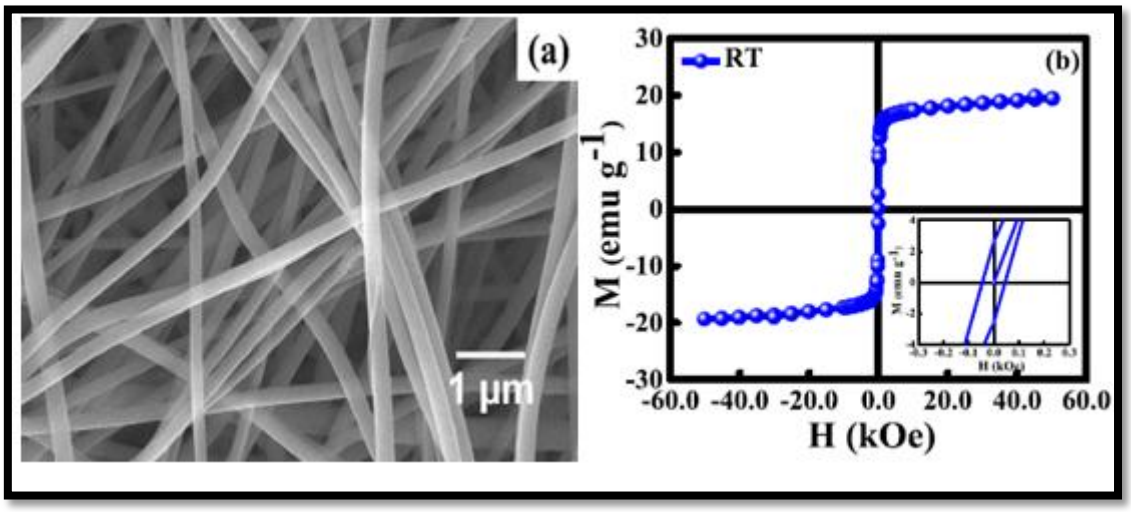

Figure 7: (a) FESEM Image of FCO Nanofibers (b) The M-H Loop at Room Temperature of FCO Nanofibers [7].

3. **$FeCo_2O_4$ nanoflakes:** The FCO nanoflakes were synthesized by hydrothermal method using stainless steel autoclave. The cyclic voltammetry curves of iron cobaltite nanoflakes at different scan rates give the capacitive value of about 433 Fg^{-1}. Also, the FESEM image shows the nanoflake morphology at 1 micron in Fig.9 [8].

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4. **$FeCo_2O_4$ microspheres and $FeCo_2O_4$ nanosheets:** Both FCO microspheres and FCO nanosheets were synthesized by hydrothermal method at different temperatures. SEM images show the clear morphological vision of FCO microspheres and FCO nanosheets in Fig.10. The FCO microspheres and FCO nanosheets both exhibit the capacitance of about 231.5Fg^{-1} and 399.0Fg^{-1} in Fig.11 [9].

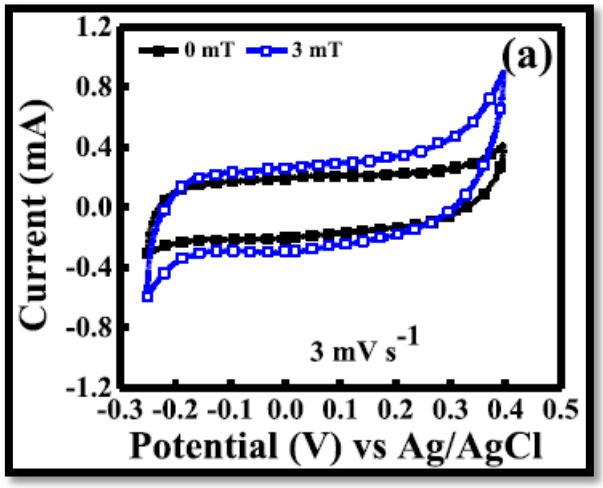

Figure 8: Cyclic voltammetry curves of FCO nanofibers [7].

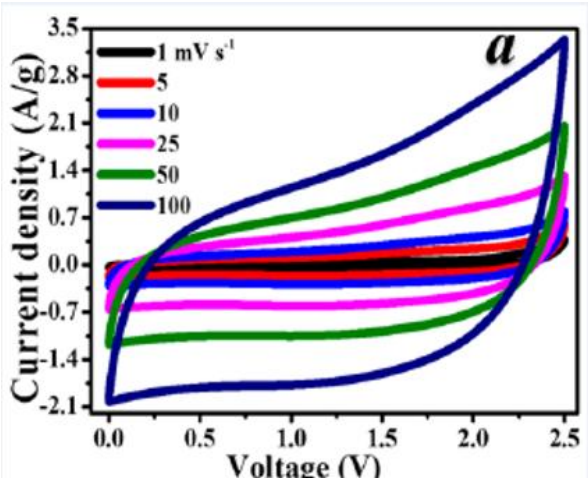

Figure 9: CV Curves of FCO Nanoflakes at Different Scan Rates

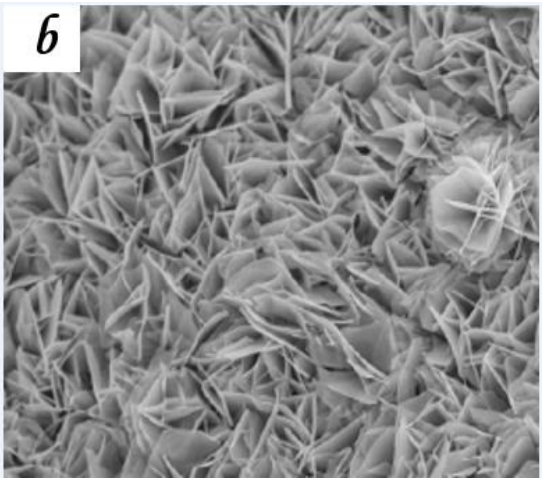

Figure 10: SEM Images of FESEM Image Showing Nanoflakes [8].

5. **$CuCo_2O_4$ (CuCO) highly ordered mesoporous nanowires:** The CuCO highly ordered mesoporous nanowires were synthesized using a silica template because it helps to increase the order of mesoporosity of nanowires. The CV curves at various scan rates reveal the most prominent supercapacitance value of about 3080 Fg^{-1}. On the other side, the TEM image shows the successful preparation of nanowires in Fig.12 [10].

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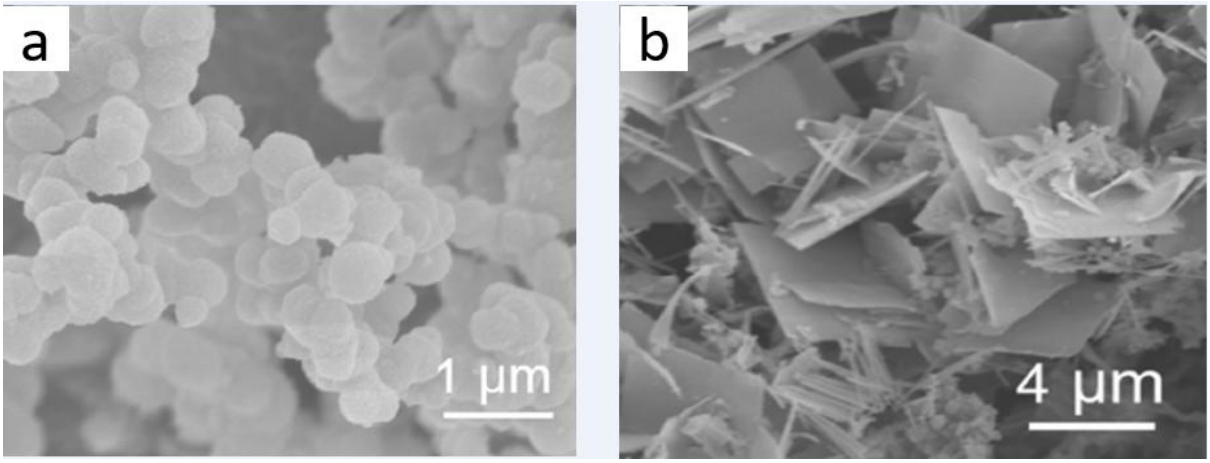

(a) FCO Microspheres **(b) FCO Nanosheets [9].**

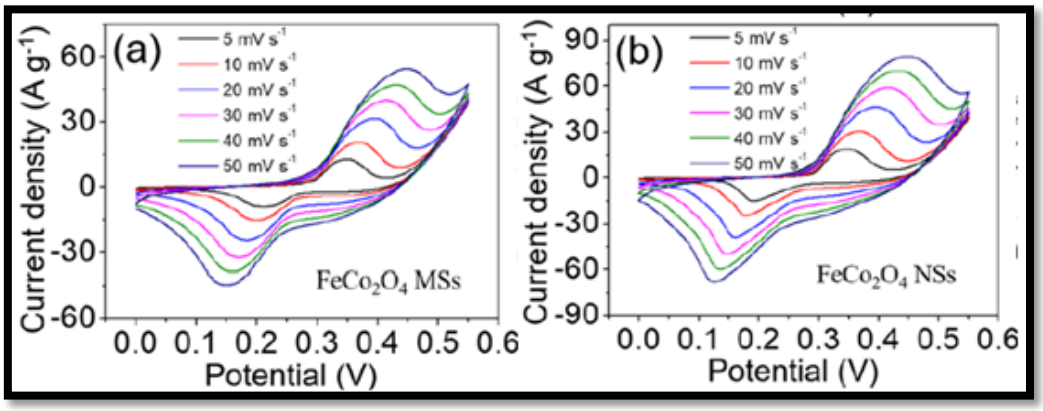

Figure 11: CV Curves of (a) FCO Microspheres and (b) FCO Nanosheets at Different Scan Rates [9].

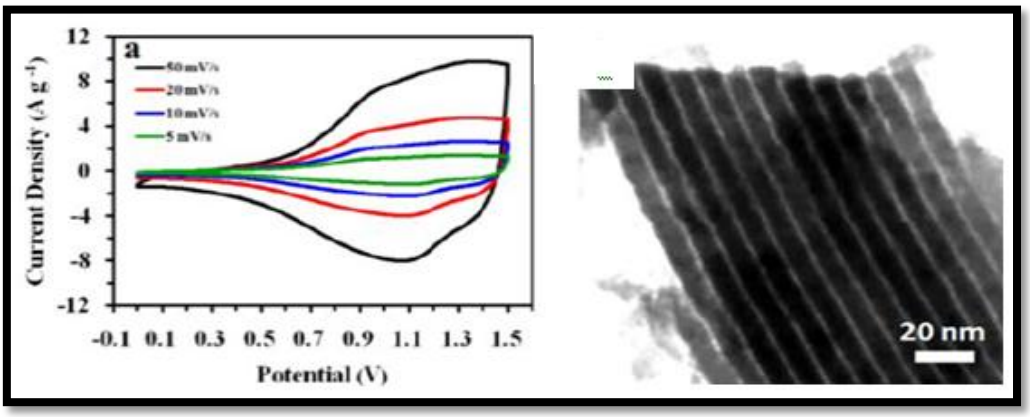

Figure 12: (a) CV Curves of Cuco Mesoporous Nanowires at Different Scan Rates (b) TEM Image of Cuco Nanowires [10].

6. **$ZnCo_2O_4$ (ZCO) nanorods:** $ZnCo_2O_4$ is considered an excellent functional material that can be applied as electrode material. The ZCO-nanorods were found to exhibit the

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supercapacitive behavior of a specific capacitance value of approximately 1400Fg^{-1} through CV curves. The TEM image shows the nanorods of zinc cobaltite at 300nm in Fig.13 [11].

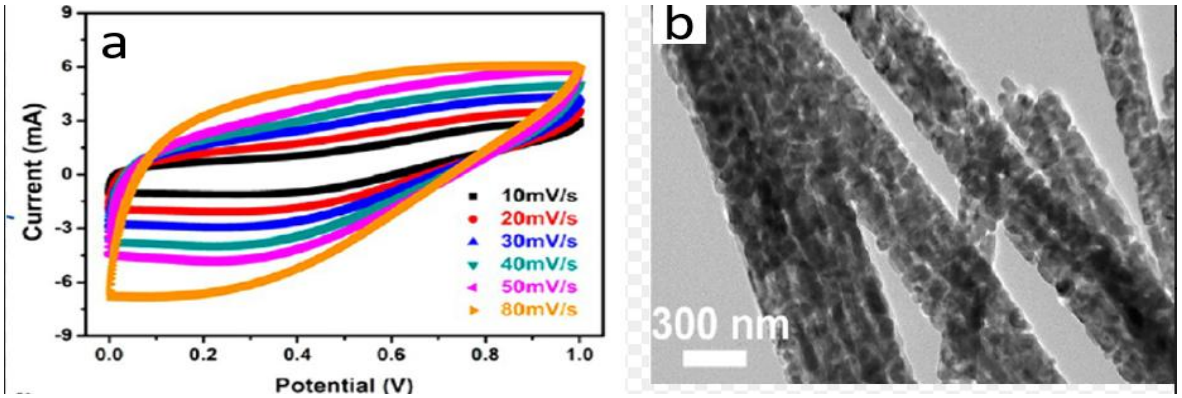

Figure 13: (a) CV Curves of ZCO Nanorods at Different Scan Rates (b) TEM Image of ZCO Nanorods [11].

7. **$NiCo_2O_4$ (NCO) mesostructured nanosheets:** Nickel cobaltite mesostructures obtained from ultrathin nanosheets (NCO-mNS) were found to result in the excellent supercapacitive value equal to 2282Fg^{-1}. Also, the TEM (Transmission electron microscopy) image shows the formation of a nanosheet at 500nm in Fig.14 [12].

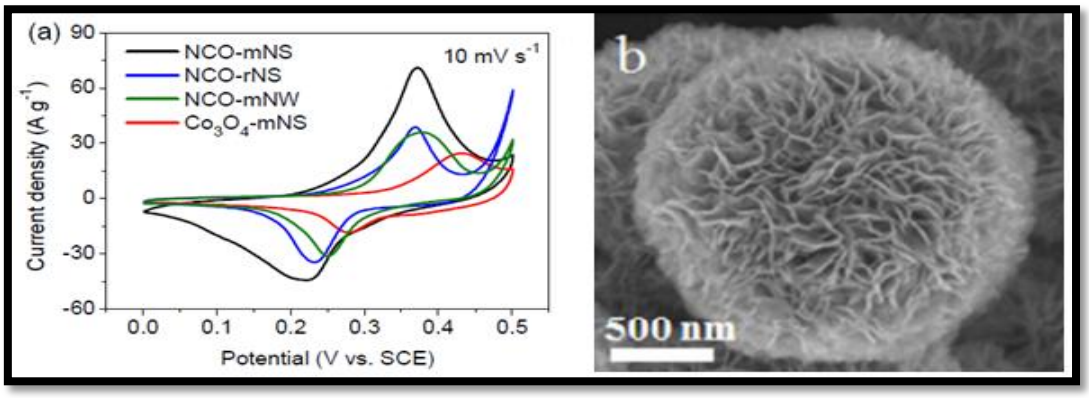

Figure 14: (a) CV Curves of NCO Nanosheets (B) TEM Image of NCO Nanosheets [12].

Table 1: List of Various Cobaltites and their Respective Capacitance Values.

Sl. No.	Cobaltites Materials	Capacitance value
1.	Nanoporous Co_3O_4 nanorods	281 Fg^{-1} [6]
2.	$FeCo_2O_4$ Nanofibers	165 Fg^{-1} [7]
3.	$FeCo_2O_4$ nanosheets	399 Fg^{-1} [9]
4.	$FeCo_2O_4$ nanoflakes	433 Fg^{-1} [8]
5.	$FeCo_2O_4$ Microspheres	231.5 Fg^{-1} [9]
6.	$CuCo_2O_4$ nanowires	3080 Fg^{-1} [10]
7.	$NiCo_2O_4$ mesostructure nanosheets	2282 Fg^{-1} [12]
8.	$ZnCo_2O_4$ nanorods	1400 Fg^{-1} [11]

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