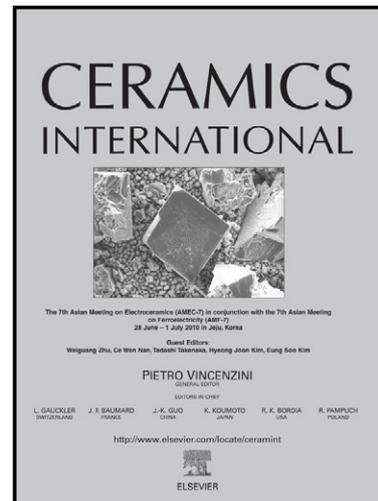


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# Recent Development in Spinel Cobaltites for Supercapacitor Application

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### Abstract

Precious metal oxides exhibit impressive characteristics that caught worldwide attention due to their promising capacitive performance, excellent electrochemical stability and low resistance, and these metal oxides have been extensively employed in supercapacitor application. This type of supercapacitors is known as redox supercapacitors or pseudocapacitors which applied faradaic process in storing energy in their systems. Thus, new materials with impressive electrochemical performance are highly demanded. In this aspect, cobaltite system with spinel structure has been the subject of intense research due to its established applications in electrochemistry. Besides, carbonaceous materials like activated carbons, carbon nanotubes, graphites, graphenes and fullerenes utilise electric double-layer capacitance whereby energy is stored by charge separation at an electrode/electrolyte interface. With greater development conducted on metal oxides and carbonaceous materials for supercapacitor application, introduction of hybrid and composite electrodes comprise of these two types of materials have been well received.

**Keywords:** B. Composites; D. Transition metal oxides; E. Electrodes; Supercapacitors

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## 1. Introduction

Depletion of fossil fuels has prompted the alarming situation in search for alternative energy storage and conversion systems. Moreover, the escalating power demand in worldwide nowadays, has ensured a lot of emphasis been placed on the development of devices with high power, high energy as well as robust in withstanding hundreds of thousands of charge/discharge cycles without degrading. Therefore, supercapacitor which is also referred to as 'electrochemical capacitor (EC)', 'double-layer capacitor' or 'ultracapacitor' is considered as an innovative technology due to its uniqueness that fills the gap between batteries and capacitors. This device possesses remarkable characteristics and is efficient and capable to combine the energy properties of batteries and the power discharge characteristics of capacitors.

Electrochemical capacitors can be categorised into two groups namely double-layer capacitors and pseudocapacitors. Electrical energy storage in the former occurs at the phase boundary between an electrode (electronic conductor) and the electrolyte solution (liquid ionic conductor) [1] with no involvement of charge transfer. Moreover, the current generated in this type of capacitor is merely a displacement current due to charge rearrangement or better known as ideally polarized electrode [2]. Fast faradaic redox reactions caused by redox-active species involving metal oxides and conducting polymers are responsible in the potential determining charge transfer reaction that induces the charge storage mechanism of pseudocapacitors [3].

At the present time, worldwide research and development focuses on enhancing the performance and ensuring the cost reduction of electrochemical capacitors. However, the crucial importance is to maintain the power capability, fulfilling the cycle life requirements as well as to increase the capacitance and energy density performance. Various ways have been developed to achieve these criteria such as mixing the metal oxides to become binary or ternary oxides, compositing the metal oxides with carbonaceous materials like activated carbons, fibres, aerogels, xerogels, fullerenes, graphite, carbon nanotubes or graphene, as well as incorporation of the metal oxides with conducting polymers. Composite electrodes involve the combination of two types of materials within the same electrode whereas hybrid electrodes comprise of two different electrodes with different materials such as metal oxides with carbonaceous materials [4]. Adopting nanotechnology in optimizing the microstructure of the electroactive materials in the electrodes has become a notable issue as the charge storage system in pseudocapacitors involve the first few nanometers from the surface [5,6]. Moreover, active material with smaller particle size may contribute to higher capacitive performance due to the larger contact area between the electrode/electrolyte in nanostructured oxides. Greater power delivery and better cycling stability can be achieved as well [7]. Undoubtedly, nanodimensional materials possess high electrical conductivity that makes them as promising energy storage systems in the current situation whereby energy demand is expanding [8]. Therefore, much research effort has been poured in to develop effective methods in the preparation of nanostructured metal oxides and hydroxides in various forms like nanoparticles, nanofibres, nanorods, nanowires, nanotubes, nanosheets and so on. In this context, cobaltite system with spinel structure has gained recognition

from worldwide researchers due to its strong establishment in the field of electrochemistry. For example, nickel cobaltite,  $\text{NiCo}_2\text{O}_4$  is one of the promising metal oxides in the family of cobaltite materials which has a spinel structure  $\text{AB}_2\text{O}_4$ , with the nickel ions reside at A-sites and cobalt ions at B-sites. The spinel structure has received much attention by numerous researchers as more than 30 ions with radii ranging from 0.5 to 1.0 Å can be incorporated in the spinel-like phases [9]. The A and B ions occupy one-eighth of the tetrahedral interstices and half of the octahedral interstices in this cubic structure ( $a \approx 8 \text{ Å}$ ).

It is known that the fundamental and physicochemical properties of cobaltite systems are dependent on the methods of preparation, composition of oxides and temperatures of thermal decomposition. When the size of cobaltite nanoparticles is reduced to the nanometer range, some of their properties can be different compared to samples in micron range. It is believed that by mixing two or more individual oxides together will lead to synergistic effects that may help in the enhancement of the performance of the synthesized materials. This helps to densify the prepared oxides with lower sintering temperature as well as to enhance the grain growth [10]. Researchers have given a considerable attention in synthesizing cobaltite system by exploring the precursors used, preparation methods, processing control and firing temperatures [11-15]. They have developed different preparative methods in synthesizing cobaltite systems not only in nanosized but in micron sized particles as well to be utilised in fuel cells [16,17], electrooxidation of phenol [18], electrocatalysis of oxygen evolution reaction [19-28], thermal decomposition of ammonium perchlorate [29], removal of toluene [30], CO

oxidation [31-33], decomposition of nitrous oxide [34], conversion of *p*-nitrophenol to *p*-aminophenol [35], gas sensors [36], batteries [37,38], electrochemical capacitors [39-51] and others. Cobaltites can be synthesized via co-precipitation [52-54], thermal decomposition [54, 55-58], sol-gel [55,57,59-62], hydrothermal [63], microwave hydrothermal [64], spin coating [65], chemical bath deposition [45,66], electrochemical deposition [67-72], electrophoretic deposition [73], plasma deposition [74], sputtering [75-77], electrospinning [78,79], spray pyrolysis [54,80], combustion [81], cryochemical [54] and so on.

This paper provides an overview of the background of supercapacitor, present commercial pursuit, current research attempts, research prospects, various energy storage systems as well as the applications of supercapacitors. Different synthesis method for the preparation of cobaltite systems and the supercapacitive performance of these materials are also reviewed.

## **2. Background of Supercapacitor**

The introduction of ‘supercapacitor’ term was initialized by Nippon Electric Company (NEC), Japan while another term ‘ultracapacitor’ was brought in by Pinnacle Research Institute, USA [82]. It is known as electrochemical double-layer capacitor (EDLC) terminologically. An electrical storage device known as ‘Leyden jar’ was developed by Ewald von Kleist in 1745 which was later on, invented by Pieter van Musschenbroek. This Leyden jar sets the prototype of all capacitors. This glass jar which was wrapped with silver or tin foil was filled with salt solution and a conductive metal

wire was immersed into it. This led to the occurrence of electrical contact in the glass jar. However, the double-layer capacitance at the interface of metal-solution was not being considered at that time. In 1749, Benjamin Franklin modified the Leyden jar and came out with the design of a 'battery' by connecting the two wires from the electrode and outside of the foil to an electrostatic machine. Electrostatic capacitor was introduced later on by designing jar with an electrode which was connected by a metal chain to the inner of the glass surface. Solution placed inside the jar was replaced with a foil lining while the external glass surface was wrapped with tin foil. In 1780, Alessandro Volta introduced metal plate capacitor with a dielectric of ebonite which was a hard rubber made of natural latex and 20-40 % sulfur [82].

Pioneer in 'dielectric' field, Michael Faraday proved the capability of dielectric material in reducing the size of a capacitor. Thus, the SI unit of capacitance, farad was named after this British physicist due to his novel contribution. According to C.F. Schönbein and W.R. Grove, electrochemical cells with two electrodes immersed in an electrolyte solution may induce the electrolysis process with power source behaviour below the decomposition voltage. The discovery of electrolytic double-layer was highlighted by Hermann von Helmholtz in 1853 while the theory of diffuse double-layer and ion adsorption was developed by G. Gouy, D.L. Chapman, O. Stern, A. Frumkin and D.C. Grahame in 1910-1950 [82]. The chronology of important milestones leading to the commercialization of the supercapacitor is listed in Fig. 1.

### 3. Present Commercial Pursuit

Since 1970s, supercapacitors has been widely applied as memory backup in computers, standby power in electronics, bicycle lighting, flashlights, alarm systems, and battery substitute for toys while in the late 1980s, the importance of supercapacitors was driven by military visions of laser weaponry, missile guidance, electric guns, all-electric tanks, and gigantic short-time pulse power sources. In the 1990s, this energy storage device is being used in the industries of power electronics, automotive, and railway for power factor correction, regenerative braking, electric vehicle load leveling as well as catalyst preheat [82]. Different technologies have been brought in to manufacture supercapacitors since 1995 with Panasonic and Maxwell Laboratories produced carbon based supercapacitors in organic electrolyte solution while Livermore National Lab designed supercapacitors using carbon aerogel that worked in aqueous system. Pinnacle Research Institute and Los Alamos National Lab developed metal oxide and conducting polymer based supercapacitors, respectively. These two types of energy storage devices worked in aqueous system [82]. Based on the historical roots of supercapacitor technology, carbon is the most utilised technology in the commercially available devices.

Production of supercapacitors has been massively carried out in worldwide especially in Japan (NEC-Tokin, Panasonic/Matsushita and Nippon Chemi-Con), South Korea (Ness Capacitor Co.), United States of America (Cooper 'PowerStor', ELNA 'Dynacap', Jeol 'Nanogate Capacitor', Evans Inc., EPCOS, Maxwell 'BoostCap', Kold Ban 'Kapower' and AVX 'Bestcap'), Canada (Tavrima), Germany (WIMA), Russia (ESMA) and Australia (Cap-XX).

Hybrid vehicles powered by a combination of internal combustion engine, generator, batteries and supercapacitors have garnered huge interests and popularity from consumers around the world. In Japan, Toyota and Honda utilise supercapacitor modules in their 'Prius' hybrid and 'FCX' fuel cell vehicles, respectively. In Germany, BMW applied the supercapacitor technology in 'SUV X 5' vehicle while MAN installed this energy storage device in a diesel electric bus in Nuremberg, Germany. Reduction in fuel consumption by 20% has been achieved in the 3-month test and lower noise emission was reported [82].

As various industries develop rapidly, the demand for electrochemical capacitors with different capacitance values is escalating. For instance, applications of electronics, digital cameras, automotive control systems, medical devices, automatic meter readers, wireless transmission, uninterruptible power supply and others require supercapacitors with 1 F to 150 F. Thus, the occurrence of loss of stored information during brief disruption in the power supply can be avoided as supercapacitors possess the capability to retain data. Moreover, it is reported that the high market demand for supercapacitors to be utilised in memory protection of electronic circuitry has led to the production of this device to about \$150-\$200 million annually [83]. Besides, it is proven that the electronic power transformer (EPT) equipped with supercapacitors energy storage system is comparable with the uninterruptible power supply (UPS) and dynamic voltage restorer (DVR) [84]. Another potential application of supercapacitors is in wireless sensor networks which is widely applied for structural monitoring of buildings and infrastructures, monitoring of greenhouse effect, air pollution and wastewater, detection

of forest fires and landslides, agricultural industry in irrigation automation, area monitoring in military surveillance, and many more [85,86].

Higher peak power applications or more energy intensive requirements in industrial power back-up, renewable energy systems and Telecom based station power back-up require supercapacitors with capacitance value ranging from 300 F to 350 F. Besides, high-end supercapacitors (650 F to 3000 F) are utilised in automotive subsystems, hybrid drive trains, rail system power and heavy transportations like buses and trucks. Moreover, with the contribution of supercapacitors, it is believed that the performance of internal combustion engines in hybrid electric vehicles may achieve the optimum state. Through the advancement of science and technology, the environment can be conserved with the introduction of low-emission hybrid cars, buses and trucks. This leads to the development of fuel cell/supercapacitors hybrid power sources for the application in electric vehicle [87]. Recently, Ayad and co-workers [88] developed a hybridized system comprising fuel cell for supplying permanent energy, supercapacitor with high power density to compensate intrinsic limitations of the main source, and battery with impressive energy density to back-up during restriction of power and energy. Therefore, studies on supercapacitors are focused on increasing specific capacitance, improving energy density and power density, and prolonging cycle life.

#### 4. Current Research Attempts

Electrochemical capacitors are prevailing not only in the scientific world but in daily applications as well. In order to develop high performance energy conversion and storage systems, assembling environmentally friendly electrode materials that exhibit impressive power and energy densities at low fabrication costs has become an emerging trend. Carbonaceous materials, metal oxides and conducting polymers have been extensively explored in supercapacitor technology. Searching for novel preparation methods in producing lower cost alternative metal oxides that exhibit great power and energy to replace ruthenium oxide as electrode material has become immense research interest among the scientists and industrialists. Moreover, developing activated carbon based supercapacitors from various raw materials such as nuts, shells, fibers and trunks which are deemed as waste materials is an ideal way leading to greener environment. Recently, sugar (sucrose) underwent the pyrolysis process followed by activation under the flow of  $\text{CO}_2$  in the preparation of sugar derived activated carbons for supercapacitor applications [89]. Being an inexpensive source, sugar becomes an appealing precursor for the preparation of activated carbon due to its uniform structure, local availability and high chemical purity. The capability of hybrid and composite capacitors to deliver high power, withstand extreme cycling and working in larger voltage range has ensured these electrode materials to become research focus. Moreover, the incorporation of organic or inorganic materials with carbon may lead to the production of new materials with outstanding physical and chemical properties for numerous applications. However,

synthesizing carbon materials with improved reproducibility and controlling the size and defect density are some of the greatest challenges for future applications [90].

Carbon nanotubes and graphite as promising supercapacitive materials have been extensively explored. Lately, a lot of emphasis is placed on graphene due to its high surface area, excellent electrical conductivity and impressive capacitance performance [91]. Therefore, research interests in exploring graphene have grown among worldwide scientists to develop superior supercapacitive materials by incorporation of graphene with multiwalled carbon nanotubes [92,93], carbon black [94], metal oxides [95-107] and conducting polymers [108-116]. Besides, the combination of graphene/metal oxide/carbon nanotubes [117], graphene/polymer/carbon nanotubes [118-120] and graphene/polymer/metal oxide [121] are believed to display some synergistic effects and exhibit impressive electrochemical performance. Thus, the attention of these researchers is drawn to the preparation routes of these ternary composites.

Utilising electrolytes that ensure wide electrochemical window, less toxicity, low flammability and high thermal stability pose as a novel approach in conserving the environment. Therefore, supercapacitor systems using aqueous, organic and polymer electrolytes have been assembled and evaluated in order to meet the demand for safe operation and high electrochemical stability besides exhibiting impressive capacitive performance. It is a challenging attempt to apply aqueous solutions which are less corrosive and hazardous as perspective electrolytes in supercapacitors due to the intense competition with other types of electrolytes that exhibit higher ionic conductivities.

Besides, less emphasis is being stressed on energy storage devices using ionic liquid electrolytes that pose to be a promising strategy in enhancing the electrochemical performance of the supercapacitors back in early 2000s. Ionic liquid is applicable above room temperature [122,123] as well as cater for high temperature applications [124]. Besides complying with safety measures, electrode materials with high capacity retention can be obtained as ionic liquids with melting points lower than 370 K possesses high ionic conductivities with non-flammable and non-volatile properties [125-128]. Moreover, high ionic concentration of ionic liquids can be applied to overcome electrolyte depletion problem [129]. Although ionic liquids like imidazolium (high conductivity) and pyrrolidinium (wide electrochemical stability window that exceeds 5 V) salts are extensively explored in supercapacitor application [130], however, metal oxide based supercapacitors receive less exposure to this type of electrolyte [131].

## **5. Research Challenges**

Global warming has become an unsettled matter and an issue of worldwide interest in this 21<sup>st</sup> century. This phenomenon causes great anxieties not only among the environmentalists as well as the public. Moreover, the diminishing manner of the fossil fuels used in large generation of electricity has speed up the severity done to the nature. As the demand for global energy escalates, immediate action or attention is essential to conserve the energy and to create advancement on the existing technologies. Thus, it is essential to develop alternative energy conversion strategies and devices instead of relying on natural resources to ensure zero-carbon emission becomes a reality. This may lead to supercapacitor technology with green concept that emphasizes on electrochemical

energy production with the invention of a device that has larger energy storage and greater power released than conventional batteries and capacitors. Development or evolution to an improved or more advanced energy conversion and storage systems can be achieved by utilising nanotechnology field in the synthesis of materials to be assembled as more efficient and robust nanostructured electrodes. Problems like power losses, low charge-discharge rates and low energy densities experienced by other storage devices would become a thing of the past. Besides, the size or mobility of supercapacitors has been well received to fit into various applications and they turn out to be convenient to handle and useful compared to gigantic systems in storing energy. Therefore, the main challenge faced by the energy experts nowadays is inventing more sustainable and environmentally friendly electrochemical energy storage devices with the hope to be living in a much cleaner and greener environment as well as a novel move to accelerate towards zero-carbon emission.

## **6. Energy Storage Systems**

Batteries, fuel cells and electrochemical capacitors are the three well-known electrochemical energy storage and conversion systems. Innovative ideas in developing more desirable or satisfactory systems are in progress with the hope that the electrochemical energy production of these systems are capable to cater for the demand of worldwide energy consumption. The basic operation mechanisms of the three systems are presented in Figs. 2-4 with two electrodes are in contact in an electrolyte solution while the energy-providing process takes place at the phase boundary of the electrode/electrolyte interface. Moreover, separation between the electron and ion

transport can be observed.

Electrical energy in battery and fuel cell is being stored indirectly whereas capacitor involves direct storage [132]. In battery and fuel cell systems, the occurrence of faradaic process at two electrodes with different electrode potentials was due to the involvement of electron transfer while in capacitor; non-faradaic process takes place as charge-transfer reactions do not occur on its plates. However, electrical energy is being stored electrostatically on the plates of a capacitor with positive and negative electric charges. Although there is no charge transfer across the interface, changes observed in the potential, electrode area and composition of electrolyte solution may cause the external currents to flow in capacitors [133].

Both batteries and fuel cells generate electrical energy using the same process, but they differ in locations of energy storage and conversion. In batteries, anode and cathode act as “active masses that are involved in the conversion of chemical energy via redox reactions and both energy storage and conversion processes occur in the same compartment. On the other hand, fuel cells utilise oxygen from air (from the environment) and fuels like hydrogen and hydrocarbons (from the tank) to be applied as “active masses” which are subjected to redox reactions, while the applied anode and cathode portray as charge-transfer media only. Thus, fuel cells comprise of two different components with energy storage in the tank and energy conversion in the fuel cell. In supercapacitors, transportation of the cations and anions of the electrolyte within the solution to the charged interfaces leads to the formation of electrical double-layers

(EDLs).

Fig. 5 represents Ragone plot with different energy contents (specific energy) and rate capability (specific power) of batteries, fuel cells and supercapacitors. Fuel cells are high-energy systems and supercapacitors possess high-power, while batteries exhibit intermediate energy and power properties. Besides, supercapacitors have drawn a wide attraction from many researchers due to their capability to combine the energy properties of batteries and the power discharge features of capacitors.

## **7. Synthesis of Cobaltites**

Various preparative methods have been employed to synthesize novel products. This involves chemical methods such as co-precipitation, sol-gel, electrochemical and solvothermal as well as traditional ceramic preparation known as solid-state route.

### **7.1. Co-precipitation**

The capability of co-precipitation in structural controlling has made this method to be widely applied in the synthesis field. The formation of nanoparticles regardless of the size and shape of the particles is depending on the operating parameters or the conditions of the crystallization process that are involved. Due to its excellent stoichiometric control and high degree of homogeneity, this method offers large-scale powder production. Besides, relative rates of nucleation and growth during the synthesis process are the contributing factors in obtaining desired size and size distribution of the products. Moreover, smaller particles can be formed by the rapid addition of the

precipitating agent like sodium hydroxide into the salt solution under continuous stirring due to larger nucleation rate than the growth rate. Bo and co-workers studied on the effect of precipitating agents like sodium hydroxide, sodium carbonate and oxalic acid in the preparation of nickel cobaltite [53]. Besides, Chi and his group of researchers synthesized cobalt cobaltite spinel via hydroxide co-precipitation in order to study on their electrocatalytic activities for oxygen evolution reaction [23]. Besides, particle agglomeration and occurrence of oxidation of nanoparticles can be avoided by coating the particles with surfactant like oleic acid followed by dispersion into medium like ethanol, methanol or ammonia [134].

## 7.2 Sol-gel

Being a soft-chemistry route, preparation of metal oxides using sol-gel method includes both chemical and physical processes such as hydrolysis, polymerization, gelation, drying, dehydration and densification [9]. This method of preparation involves the formation of 'sol' and 'gel', whereby the evolution of inorganic route based on aqueous solutions of metal salts like chloride, oxychloride and nitrate or the metal-inorganic route based on metal alkoxides in organic solvents formed a colloidal suspension (sol) followed by the gelation of the sol to form a network in a continuous liquid phase known as 'gel' [135]. With the capability of producing nanoparticles (unsupported) as well as coated layers (supported), therefore, sol-gel route is widely approached and extensively explored by various researchers. Moreover, by tuning the synthetic parameters such as hydrolysis temperature, reaction pH, hydrothermal treatment, solvent removal step and calcination, this wet chemical method promises

nanosized and better morphological control of the functional materials. Wu and co-workers has successfully prepared nickel cobaltite with coral-like porous crystals, nanoparticles and submicron-sized particles via sol-gel route using citric acid as the chelating ligand by controlling parameters like initial concentration of reactants, solvent species and reaction time [60].

### **7.3 Electrochemical Methods**

Electrochemical methods like cathodic electrodeposition and anodic electrodeposition have been employed in synthesizing cobaltite samples on different substrates like nickel foam [67,68], stainless steel sheet [69], nickel foil [70,71], iron foil [70], graphite [72] and so on. The electrodeposition process can be conducted in a standard three-electrode electrochemical cell consists of the coated substrate as the working electrode, platinum as counter electrode, and saturated calomel electrode (SCE) [67], Hg/HgO [68,70,71] or Ag/AgCl [69,72] as the reference electrode. Besides, deposition of thin film samples is affected by various parameters such as applied potentials, concentration of the electrolyte, pH and deposition time. Thus, this method is capable to produce sample that is homogeneously coated onto a specific area of the substrate.

### **7.4 Solid-State Route**

Solid-state route involves heating or sintering at high temperatures of the ground precursors in the form of oxides, carbonates, oxalates or other compounds which consist of the desired metal elements. It will be practical or useful to have the knowledge of phase diagram of the synthesized samples with desired compositions in order to reach

optimization of the preparative conditions. Besides, the synthesizing job will be more efficient by conducting intermittent grinding between the heating cycles. Song and co-workers [136] prepared binary Zn-Co spinel oxide via solid-state route by mixing zinc and cobalt acetates in molar ratio 1:2 with oxalic acid acting as the chelating agent.

## 8. Cobaltites based Supercapacitors

Researchers have immersed deeply into research works on cobalt oxide based supercapacitors due to its impressive capacitive performance as reported by Gao et al. [47] and Xu et al. [48] in exhibiting specific capacitance value of  $746 \text{ F g}^{-1}$  and  $574 \text{ F g}^{-1}$  at a current density of  $5.0 \text{ mA cm}^{-2}$  and  $0.1 \text{ A g}^{-1}$ , respectively. Meanwhile, Kandalkar et al. [44] and Hu and Hsu [136] developed cobalt oxide electrode that displayed highest specific capacitance value of approximate  $235 \text{ F g}^{-1}$  and  $230 \text{ F g}^{-1}$ , respectively. With the increasing number of researchers who have huge interest in developing cobalt oxide electrodes over the years, Kandalkar et al. [49] is able to produce this metal oxide based supercapacitor that exhibited specific capacitance value of  $118 \text{ F g}^{-1}$ , while Wang et al. [137] obtained cobalt oxide that yielded high specific capacitance of  $102 \text{ F g}^{-1}$  at the scan rate of  $3 \text{ mV s}^{-1}$  in  $4.0 \text{ M KOH}$  electrolyte by utilising mesoporous silica material MCM-41 as a template in producing this metal oxide. Zheng et al. [138] also came out with an idea of preparing  $\text{Co}_3\text{O}_4$  using mesoporous silicas, KIT-6 and SBA-15 as templates. They found that the highest specific capacitance of  $370 \text{ F g}^{-1}$  can be achieved at a current density of  $0.5 \text{ A g}^{-1}$  using  $\text{Co}_3\text{O}_4$ -KIT-6 synthesized at the hydrothermal temperature of  $40 \text{ }^\circ\text{C}$  and calcination at  $200 \text{ }^\circ\text{C}$ . Besides, Cui et al. [139] produces  $\text{Co}_3\text{O}_4$  nanorods via microwave-assisted hydrothermal method with cetyltrimethylammonium bromide

(CTAB) acting as a template. The prepared material was found to deliver maximum specific capacitance of  $456 \text{ F g}^{-1}$ .

This capacitive performance was derived from the electrochemical process involving  $\text{Co}_3\text{O}_4$  and the electrolyte system whereby redox peaks were observed in cyclic voltammetry analysis. The possible mechanism can be written as follow [48,140,141]:



Synthesis of cobalt oxide can be conducted by various methods such as microwave irradiation [142], potentiostatic deposition [143], solvothermal [144-146], sol-precipitation [147,148], sol-gel [149], hydrothermal [148,150], chemical bath deposition [66], ammonia-evaporation-induced method [151], spray pyrolysis [152], microemulsion (reverse micellar) [153], polyol process [154], thermal decomposition [155], radio frequency sputtering [156], pyrolysis of an organometallic precursor, cobalt 2-ethylhexanoate [157] and others. A template-free synthesis method was attempted by Gao et al. [47] in preparing  $\text{Co}_3\text{O}_4$  nanowire arrays supported on nickel foam substrate for supercapacitor application. With the absence of binders and conducting materials, this group of researchers developed working electrodes by utilising nickel foam as a support for  $\text{Co}_3\text{O}_4$  nanowires, while at the same time act as current collector in the electrochemical testing. The synthesized sample exhibits high specific capacitance of  $746 \text{ F g}^{-1}$  at a current density of  $5 \text{ mA cm}^{-2}$  due to the good interaction and well distribution of each nanowire onto the nickel foam. By adjusting the reaction conditions of producing  $\text{Co}_3\text{O}_4$  nanostructures, Xiong et al. [158] came out with a unique way of preparation by

using ethanolamine (EA)-assisted method that produces different morphologies like nanosheets and microspheres. Besides, the capability of EA in ensuring tunable morphology was highlighted as other alkali media like diethanolamine, triethanolamine or ammonia may have resulted in irregular morphology of the final product. It was reported that  $\text{Co}_3\text{O}_4$  nanosheets display better electrochemical performance than  $\text{Co}_3\text{O}_4$  microspheres by exhibiting  $92 \text{ F g}^{-1}$  at the current density of  $5 \text{ mA cm}^{-2}$  due to its larger micropore area with more diffuse structure compared to the latter.

By using a mixed solution of sodium hydroxide, hydrogen peroxide, cobalt sulfate and polyacrylamide, Cao et al. [159] proposes a very unique method in synthesizing loose-packed, mesoporous nanocrystalline  $\text{Co}_3\text{O}_4$ . Heat treatment at  $70 \text{ }^\circ\text{C}$  with the heating rate of  $1 \text{ }^\circ\text{C min}^{-1}$  was conducted on the formed gel to obtain floccules that underwent centrifugation and heating later. It was reported that impressive pseudocapacitance or electric double-layer capacitance performance can be observed in samples with the pore size of around  $8$  to  $50 \text{ \AA}$ . Thus, the synthesized  $\text{Co}_3\text{O}_4$  ( $160 \text{ }^\circ\text{C}$ ) with high surface area at approximate  $212 \text{ m}^2 \text{ g}^{-1}$  and effective pore size distribution of  $88\%$  in the range of  $10$  to  $50 \text{ \AA}$  and  $50\%$  in the range of  $20$  to  $50 \text{ \AA}$ , displays promising specific capacitance of  $401 \text{ F g}^{-1}$  in  $2.0 \text{ M KOH}$ . Moreover, it was highlighted that mesoporosity contributes to the easy penetration of  $\text{OH}^-$  electrolyte.

Besides cobalt oxide that may serve as a supercapacitive material, the nominal composition,  $\text{NiCo}_2\text{O}_4$  in nickel cobaltite subsolidus system,  $\text{Ni}_x\text{Co}_{1-x}\text{O}_y$  appeared to be one of the promising candidates due to its high electrical conductivity and desirable

optical properties in the infrared regions [76]. Moreover, it is commented that incorporation of nickel into cobalt oxide may lead to further enhancement of the electrical conductivity of the prepared samples [160,161] as well as exhibiting improvement on the initial coulombic efficiency [162]. However, there appear limited studies on  $\text{NiCo}_2\text{O}_4$  for energy storage in supercapacitors.

It was revealed that Ni-Co oxide exhibits low resistance and high reversible characteristics by displaying excellent charge-discharge properties even at high current density when tested in 6.0 M KOH [163,164]. Besides, the impressive electrochemical capacitive performance of spinel nickel cobaltite aerogels in 1.0 M NaOH in the potential range of -0.1 to 0.55 V was highlighted by Wei et al. [46]. Salunkhe et al. [45] developed nickel-cobalt oxide films on indium tin oxide (ITO) glass substrates by applying chemical bath deposition technique. Comparison between two different synthetic processes namely continuous growth process and template growth process was made by this group of researchers. In continuous growth process, formation of nickel-cobalt hydroxide with nanoflake structures was obtained by immersing ITO glass into a heated mixed solution of nickel nitrate and cobalt chloride at 70 °C until it reached a thickness of approximate 2  $\mu\text{m}$  followed by heat treatment at 300 °C for 3 hours. On the other hand, template growth process involves immersing the ITO glass into the mixed solution of nickel nitrate and cobalt chloride that was heated at 70 °C for 15 minutes before drying the coated substrate. The next step was immersing the nickel-cobalt hydroxide coated ITO glass (acted as a template) into the previous metals solution until the completion of deposition of a thick nickel-cobalt hydroxide nanorod film. The final step in this synthesis procedure

was annealing at 300 °C for 3 hours. The electrochemical performance of these two synthesized samples was tested in 2.0 M KOH at the scan rate of 20 mV s<sup>-1</sup> in the potential range of 0 to +0.5 V vs Ag/AgCl. Nickel-cobalt oxide nanorod film with the ability to facilitate fast ionic transport due to its large mesoporosity and capability to retain acceptable volume of electrolytes during the charging and discharging processes as it has large channels between the nanorods was found to exhibit higher capacitive performance than nanoflake film.

## 9. Cobaltites/Activated Carbon Supercapacitors

Drawbacks faced by supercapacitors that are incorporated with either carbon materials or metal oxides can be overcome by the combination of high specific surface area of the former with the electroactive characteristic of the latter. It is believed and proven that the ability of supercapacitors can be optimized to the fullest by combining these two materials. In general, high resistivity is a serious drawback faced by metal oxides to be utilised as electrode materials for supercapacitors. Therefore, improvement on the charge storage behaviour can be carried out by enhancing the conductivity of the electrode. In this context, the simplest way to achieve optimization of electrochemical capacitance of metal oxides is by introduction of activated carbons. This is due to the porous structure of activated carbon that may facilitate the accessibility of the electrolyte into the bulk film [165].

Thus, combination of EDLC-pseudocapacitance system is believed to enhance the overall capacitive performance of the material [166-168], improve the energy density

performance [169] and achieve long term electrochemical stability [170]. Besides, activated carbon is expected to facilitate ionic transportation to the bulk and surface of metal oxide [167,168]. Hence, activated carbon may act as support matrix to improve the dispersion of the active component and this leads to the enhancement of the electrochemical performance of the metal oxide. Incorporation of carbon materials like activated carbon (AC), carbon nanotubes (CNTs), carbon nanofibers, carbon aerogel, graphite or graphene with different cobaltites as shown in Table 1 has obtained the interests of various researchers.

Incorporating or compositing the metal oxides with carbonaceous materials can be conducted by various ways in ensuring homogeneity as well as maximizing the electrochemical capacitive of the composites. This leads to the development of different methods by worldwide researchers such as chemical co-precipitation [176-180], sol-gel [181-183], colloidal method [184], thermal decomposition [185], hydrothermal [186,187], impregnation [188-190], immersion [191], dip-casting [192], cycle voltammetry deposition [147,193], pulse potential electrochemical deposition [193], electrophoretic deposition [194,195], microwave irradiation [96,101,196,197] and radio frequency magnetron sputtering [198].

Fan et al. [174] applied thermal decomposition method in synthesizing nickel-cobalt oxides/carbon nanotube composites for supercapacitor application. Comparison in terms of capacitance values was made between nickel-cobalt oxides/CNT, cobalt

oxide/CNT and nickel oxide/CNT electrodes. It can be observed that the sequence of the capacitance performance is as below:

Nickel-cobalt oxides/CNT (Ni/Co molar ratio 1:1) electrode » nickel oxide/CNT electrode  $\approx$  cobalt oxide/CNT electrode

This binary nickel-cobalt oxide exhibits remarkable charge-discharge properties even at high current density and displays promising cycle stability by achieving 99.8% capacity retention at 1000<sup>th</sup> cycle. Moreover, this sample portrays superior electrochemical stability with a decrement of 3.6% in specific capacitance from the 1000<sup>th</sup> to 2000<sup>th</sup> cycle. The methods of preparation, supercapacitor cell configurations and supercapacitive performance of nickel-cobalt oxide/carbon composites as electrode materials for supercapacitors are tabulated in Table 2.

## Conclusion

It is undeniable that power demand, utilization in various applications, cost optimization and capacitance performance has been proven by many outstanding and prominent researchers to be crucial to the supercapacitor industry. This has led to the development of electrochemical capacitors that possess several advantages in terms of their charge/discharge efficiency, energy density, power density and lifetime (cycle number). Besides, various techniques can be attempted in the synthesis of Co-based oxides. However, the selected methods should be able to produce materials with controllable particle size that can cater for supercapacitor applications. Therefore, nanodimensional materials have received tremendous acceptance due to their capability to enhance the capacitive performance of the supercapacitor systems while maintaining

high cycle life and great kinetic reversibility. On the other hand, the potential of carbonaceous materials like activated carbon, carbon nanotubes, graphite and graphene in supercapacitor application should be taken note of. Activated carbons derived from wastes materials like oil palm shells, coconut shells, rice hulls, sawdust and wood may pose as an effective way to curb the disposal issue for the conservation of the environment. Nowadays, combination of carbons with metal oxides to form composite or hybrid supercapacitors may portray as another interesting alternative or remarkable breakthrough in this energy related applications. Such supercapacitors are incomparable in terms of their storage capabilities when these active materials are being used alone.

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**Figure Captions**

- Fig. 1.** The chronology of important milestones towards the commercialization and applications of the supercapacitor.
- Fig. 2.** Operation mechanism of a battery.
- Fig. 3.** Representation of a fuel cell.
- Fig. 4.** Scheme of an electrochemical capacitor (supercapacitor).
- Fig. 5.** Comparison between various electrochemical energy conversion systems with combustion engine, gas turbine and conventional capacitors.

**Table 1**

**Metal oxides that were incorporated with carbon materials like activated carbon (AC), carbon nanotubes (CNTs), carbon nanofibers, carbon aerogel, graphite or graphene.**

Metal Oxides	References
Cobalt oxide	Ji et al. [171]; Yan et al. [99]; Shan and Gao [172]
Ruthenium-cobalt oxide	Kim et al. [173]
Nickel-cobalt oxide	Fan et al. [174]; He et al. [175]

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**Table 2**

**Preparation methods, supercapacitor cell configuration and supercapacitive performance of nickel-cobalt oxide/carbon composites as electrode material for supercapacitors.**

Preparation Methods and Conditions	Supercapacitor Cell Configuration	Specific Capacitance (F g <sup>-1</sup> )	References
<p><u>Thermal decomposition</u></p> <p>(i) Substrate: Graphite,            (ii) Carbon nanotubes (CNTs) were grown on graphite substrate via chemical vapour deposition,            (iii) 1 μL of 2 M Ni(NO<sub>3</sub>)<sub>2</sub> + 2 μL 2 M Co(NO<sub>3</sub>)<sub>2</sub> was dripped onto the coated CNT/graphite,            (iv) The prepared electrode nickel-cobalt oxide (Ni/Co molar ratio 1:1)/CNT was subjected to heating at 250 °C for 2 hours in air.</p>	<p>Nickel-cobalt oxide/CNT            1.0 M KOH/Pt            (0 to 0.5 V)</p>	<p>569            (10 mA cm<sup>-2</sup>)</p>	<p>Fan <i>et al.</i>            [174]</p>
<p><u>Electrodeposition</u></p> <p>(i) Substrate: Nickel mesh,            (ii) Carbon nanotubes (CNTs) were grown on nickel mesh substrate via electrophoretic deposition,            (iii) 0.1 mol L<sup>-1</sup> solution containing Ni(NO<sub>3</sub>)<sub>2</sub> + Co(NO<sub>3</sub>)<sub>2</sub> at different mol ratios of Ni/Co = 8:2, 6:4, 4:6 and 2:8 was anodically deposited onto the coated CNT/nickel mesh at a current density of 3 mA cm<sup>-2</sup> for 20 seconds,            (iv) The prepared cobalt and nickel mixed oxides/CNT was subjected to heating at 300 °C for 1 hour at the heating rate of 5 °C min<sup>-1</sup>.</p>	<p>Cobalt and nickel mixed oxide/CNT            1.0 M KOH/Pt            (-0.15 to 0.50 V)</p>	<p>1024            (2 mA cm<sup>-2</sup>) for Ni/Co(4:6)/CNT</p>	<p>He <i>et al.</i>            [175]</p>

Fig. 1.

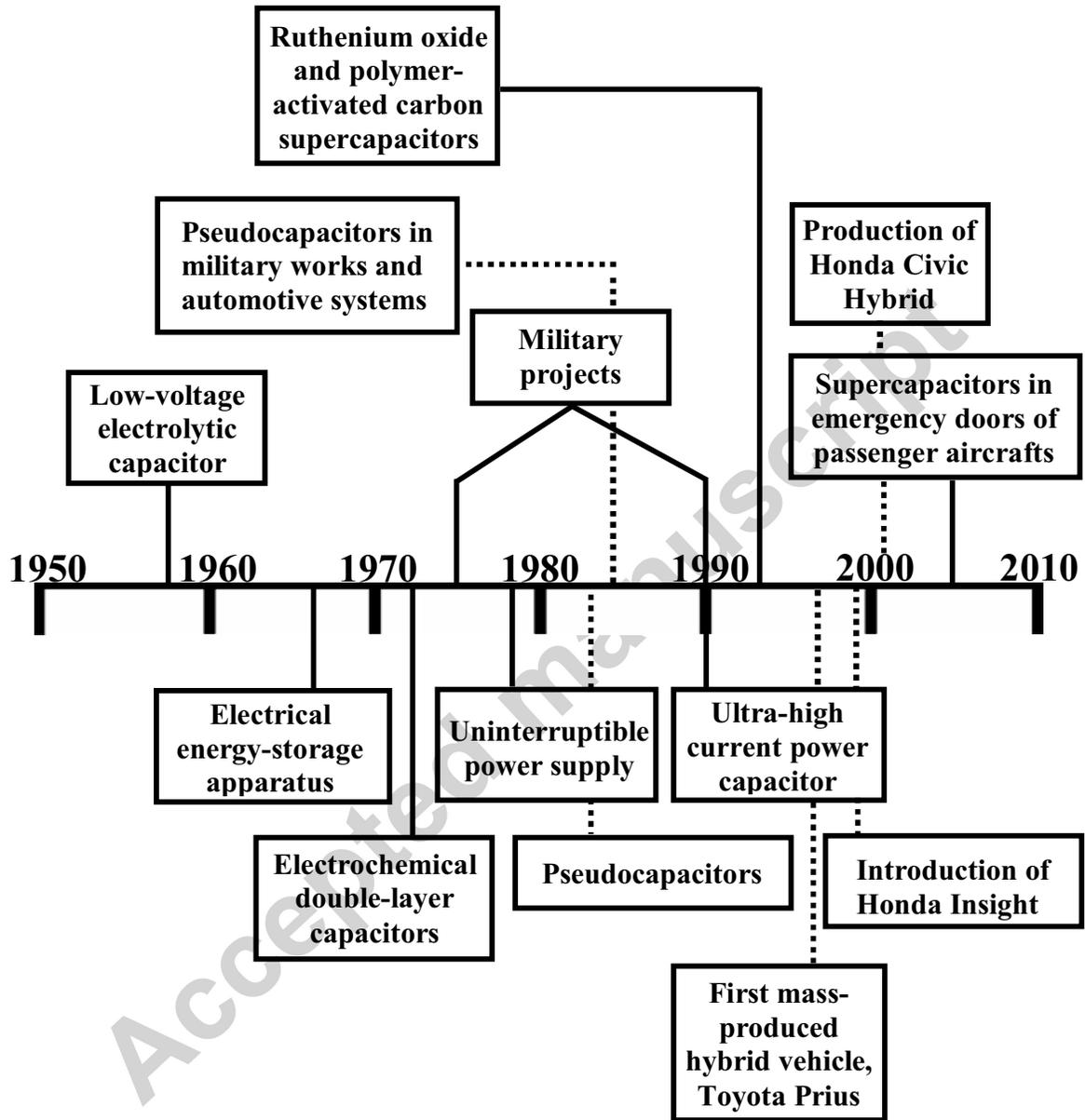


Fig. 2.

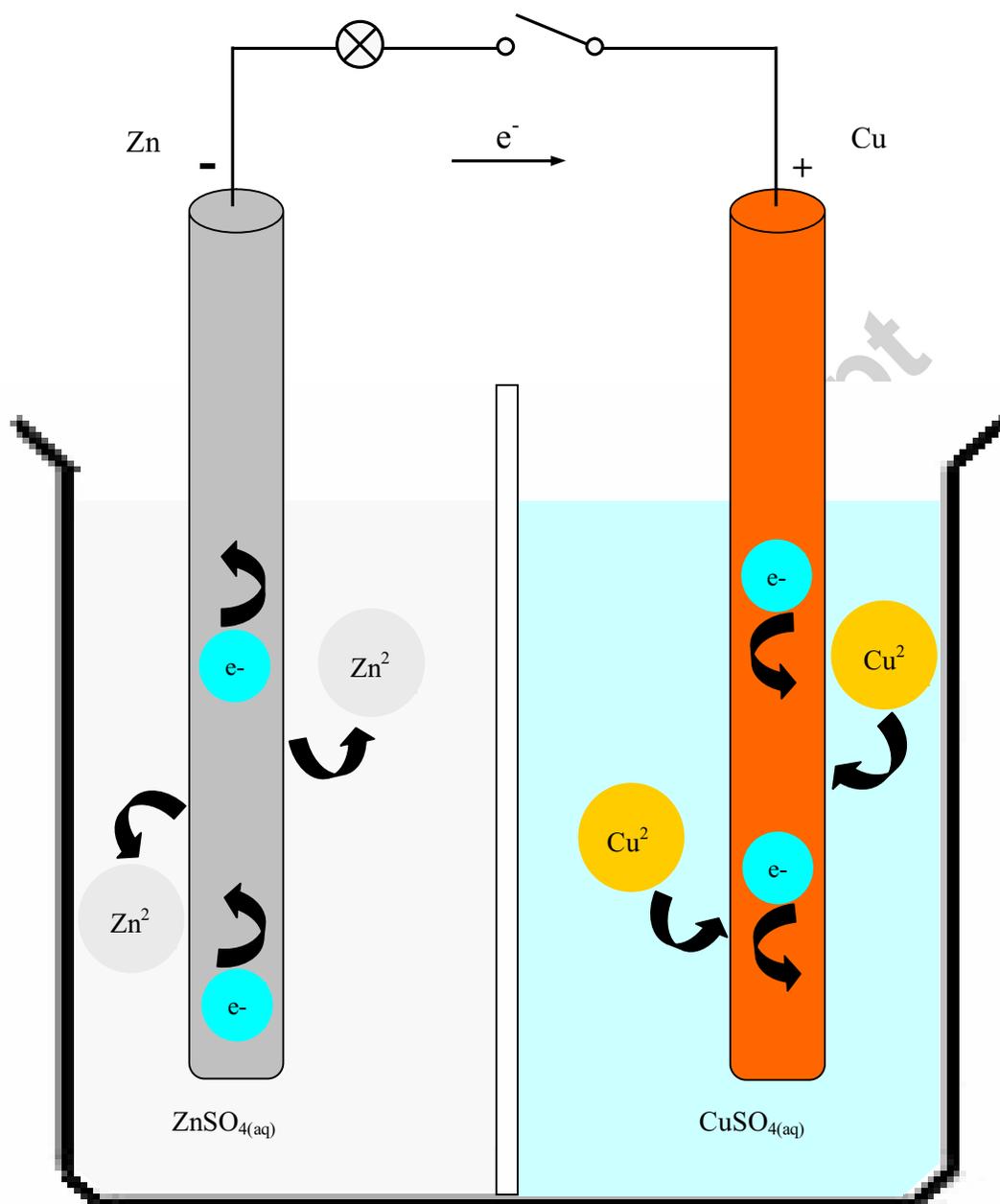


Fig. 3.

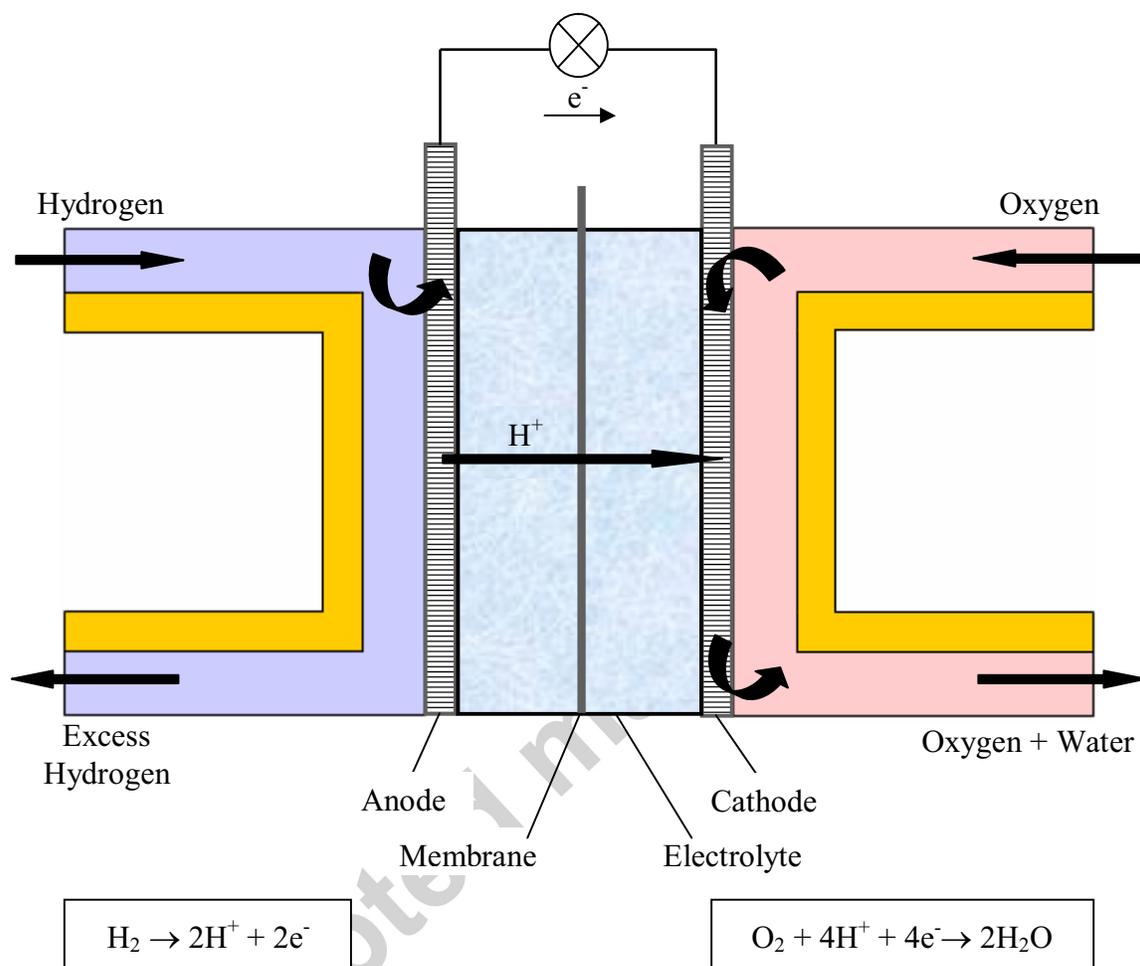


Fig. 4.

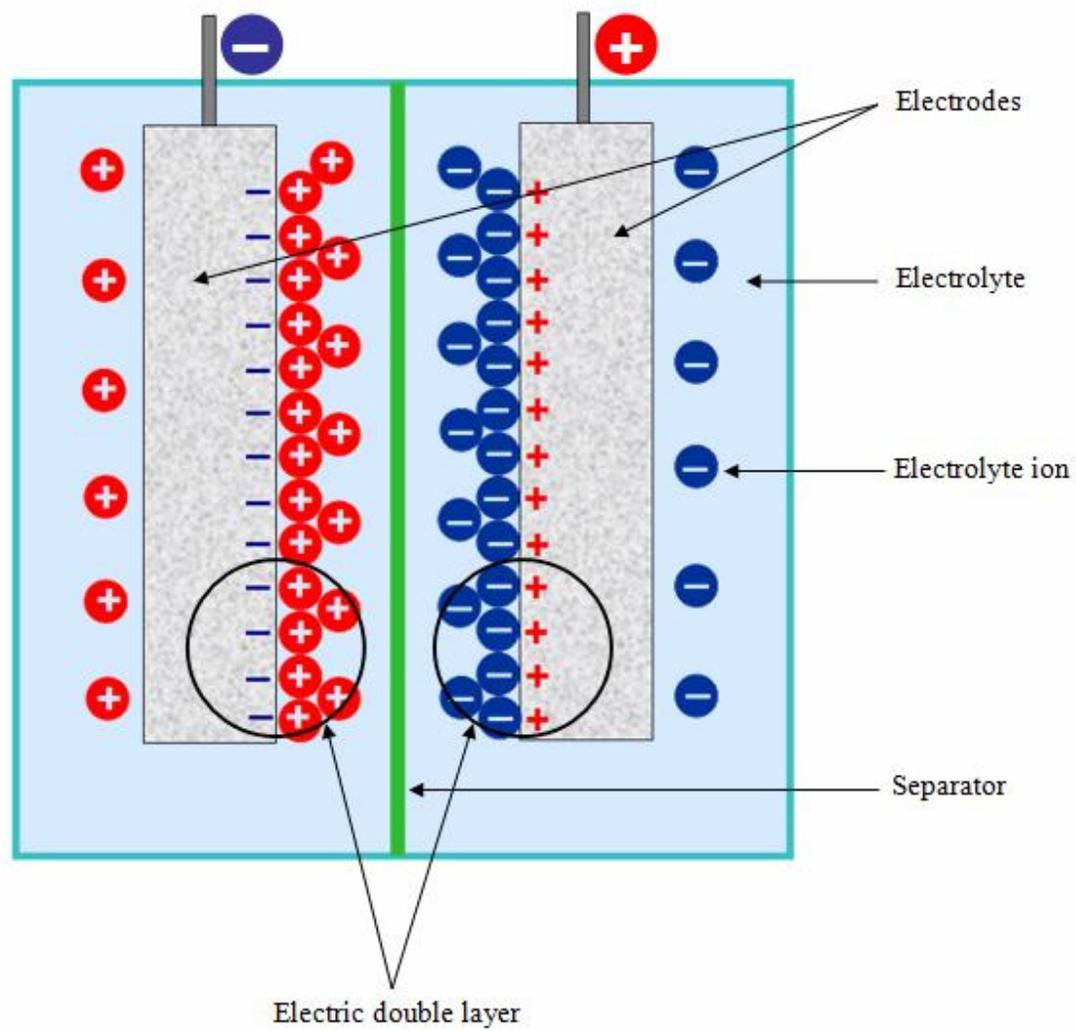
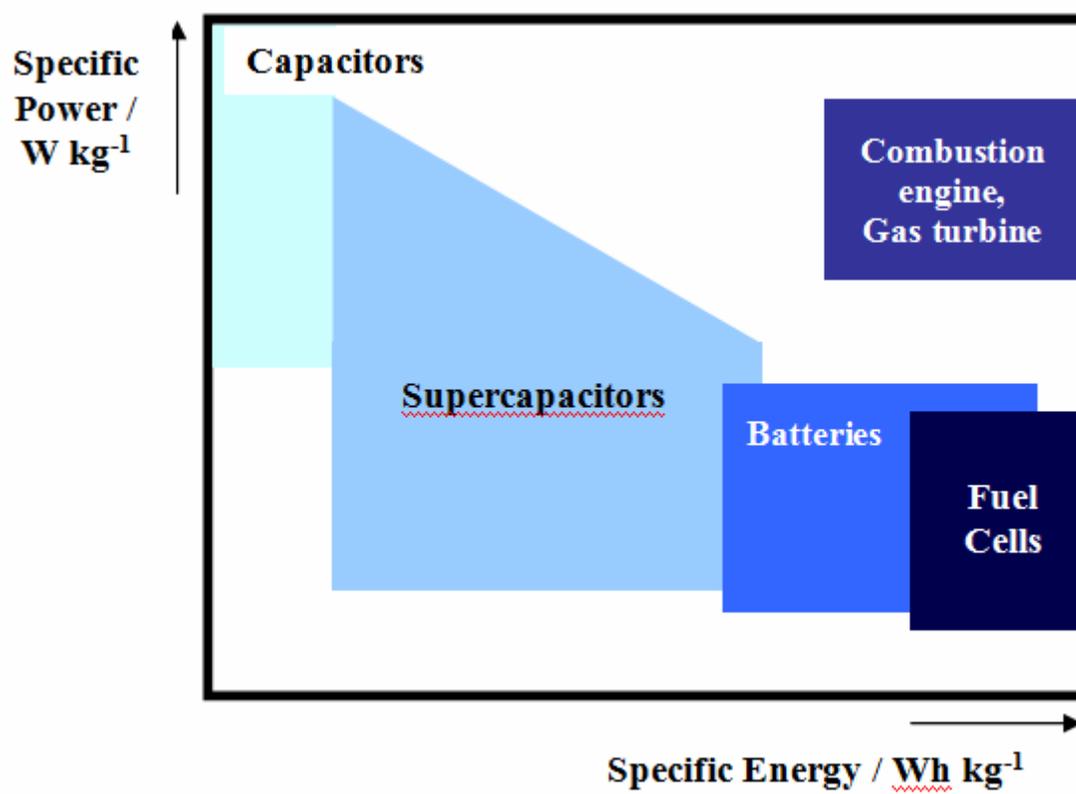


Fig. 5.



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