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Metal oxide-based supercapacitor: A review

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 V_2O_5

ABSTRACT

In the current scenario of the growing world, the requirement of non – conventional energy sources having high density & power has very much increased. Supercapacitors are showing successful energy storage devices having long life cycles, high specific capacitance & power densities. Supercapacitor performance is decided with help of electrode materials. Among the different materials of supercapacitor electrodes, in recent years research is focusing on the synthesis of metal oxides/ hydroxides and their composites, carbon metals, and polymers. Metal oxides such as In_2O_3 , Co_3O_4 , NiO , Bi_2O_4 , Fe_3O_4 , V_2O_5 etc. were widely used as supercapacitor electrode materials for storing energy. In the given paper, we are exploring the detail of metal oxide material for supercapacitor electrodes & their composites with a simple chemical method. We also explained the basic parameters involved in supercapacitor studies and the advantages of the electrochemical deposition technique through analysis of the literature.

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1. Introduction

Limited sources of fossil fuels along with growing population and technology development put the mankind in front of an energy problem. Increasing pollution forces us to think about energy and the approach to energy management. There are two main types of energy sources, fully controllable power plants (nuclear power stations, incineration plants, fossil fuels, biomass, geothermal) and renewable energy sources, which are non-dispatchable (wind and solar energy). The world human population cannot use only renewable energy sources, at least in the near future. The share of renewable energy among other types of energy sources in 2015 is shown in Fig. 1.

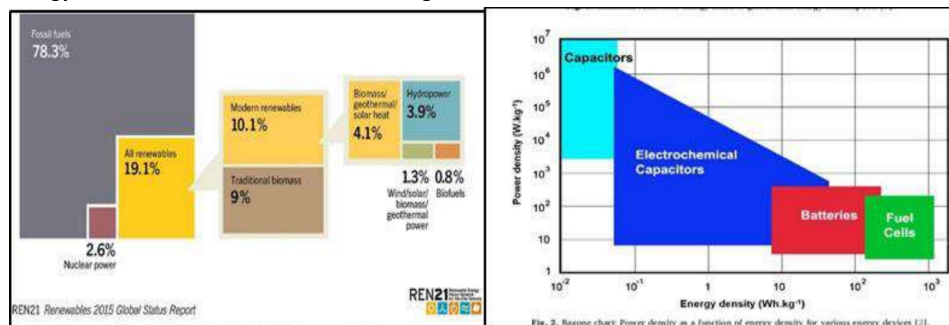


Fig. 2. Ragone chart: Power density as a function of energy density for various energy devices [1].

In the ideal case, renewable energy should cover 100% of world energy consumption, but it is only a theoretical idea that is not possible to be achieved. We should however increase the proportion of renewable energy sources in the world energy production as fast as possible. Energy from renewable energy sources needs to be (due to its non-dispatchability) stored and used when needed. Energy storage

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and accumulation is the key part of renewable energy sources utilization. Use of batteries or special hydropower plants is the only way how can we today store the energy from renewable energy sources. There are other experimental alternatives – storing energy in superconducting magnetic energy storage systems (SMES), which store it in a magnetic field created by the flow of current in a superconducting coil that has been cryogenically cooled to a temperature below its superconducting critical temperature. There are also other energy storage systems still in the phase of basic research, so they cannot be considered as regular energy storage systems. Another important step to decreasing pollution and keeping sustainable development of population is reducing emissions produced by combustion engine vehicles and replacing them with electric vehicles. Autonomy electric vehicles, which do not have connection to the electrical grid, also need to store electric energy in batteries. Using batteries, especially lithium-ion batteries, is a widely discussed and technologically developed topic. Supercapacitors could be considered as an alternative to conventional batteries for electric vehicles.

This paper is related to supercapacitors, it provides their brief description, operation principles, types and recent development. Electrochemical capacitors, also named supercapacitors or ultracapacitors, are electrical components that are able to store and accommodate certain amounts of energy. The development of supercapacitors started in the 50 s of the 20th century. First experiments started between 50 s and 70 s and were conducted by US companies General Electric (GE) and Standard Oil of Ohio (SOHIO). These first electrochemical supercapacitors reached the capacity around 1F. This type of supercapacitors was patented in 1971 by SOHIO. The first supercapacitor named “Gold Cap” was released to the commercial market in 1982 by Panasonic and had high equivalent series resistance (ESR). In 1982, first electric double-layer capacitor (EDLC) supercapacitor was developed for military purposes by the Pinnacle Research Institute (PRI). This first EDLC supercapacitor already had a low ESR. After ten years, in 1992, Maxwell Laboratories introduced to the commercial market a wide range of EDLC supercapacitors with low ESR named “BoostCap” with nominal capacity of 1 kF. Since 2007, the development of novel hybrid-supercapacitors took place. This kind of supercapacitors should reach higher nominal voltage along with higher volumetric and gravimetric energy density than conventional EDLC supercapacitors. Most of today’s supercapacitors have capacity over several thousand Farads and can provide charge-discharge currents in the range from tenths to hundredths of Amperes. Their main advantage from the application point of view is extremely high current (in comparison to batteries) that they are able to operate with. Thanks to this characteristic property, supercapacitors fill the void gap among energy storage devices between batteries (accumulators) and common capacitors (see Fig. 2 below). Supercapacitors are used in applications, where is need to store or release huge amount of energy in a very short time. Nowadays, the supercapacitors are used primarily in Hybrid Electric Vehicles (HEV), Electric Vehicles (EV) and Fuel Cell Vehicles (FCV) like passenger cars, trains, trolleybuses. Another area of supercapacitors’ use are electronic devices as Uninterruptible Power Supplies (UPS) and volatile memory backups in PCs. Third area of use are energy harvesting systems, solar arrays or wind turbines, where supercapacitors play a supplementary role next to conventional batteries [1–14]. Especially the application of supercapacitors in automotive industry brings many advantages. Supercapacitors can be used to increase the efficiency of hybrid electric vehicles in several ways. Today’s hybrid vehicles typically turn off the engine completely when the car stops, and then very efficiently start it again using energy stored in supercapacitors. There are over 600 thousands HEVs that use supercapacitors in their stop-start systems. Some supercapacitor manufacturers designed replacements for conventional vehicle batteries using supercapacitors connected across a smaller lead acid battery. The concept of their application is in the moments when the power demand peaks, such as starting a car, and they decrease the overall energy consumption from the batteries. Batteries last much longer when the discharge is small and steady. Supercapacitors in this “hybrid lead-acid battery” configuration essentially smooth out the energy demands on the battery.

A large number of review articles including a special issue by The Electrochemical society [15-27]. The capacitance of a device is largely dependent on the characteristics of the electrode material;

particularly, the surface area and the pore-size distribution [28]. The operating voltage of supercapacitors is usually dependent on electrolyte stability. Aqueous electrolytes, such as acids (e.g., H_2SO_4) and alkalis (e.g., KOH) have the advantage of high ionic conductivity (up to 1 S cm^{-1}), low cost and wide acceptance however; they have the inherent disadvantage of a relatively low decomposition voltage of 1.23 V [29]. Non-aqueous electrolytes allow the use of cell operating voltages above 2.5 V. Non-aqueous electrolyte mixtures such as propylene carbonate or acetonitrile, containing dissolved quaternary alkyl ammonium salts have been employed in many commercial supercapacitors. The electrical resistivity of non-aqueous electrolytes is, however, at least an order of magnitude higher than that of aqueous electrolytes and therefore the resulting capacitors generally have a high internal resistance [28]. In supercapacitors, a number of sources contribute to the internal resistance and are collectively measured and referred to as the equivalent series resistance, or ESR. Contributors to the ESR of supercapacitors include: (i) electronic resistance of the electrode material, (ii) the interfacial resistance between the electrode and the current collector, (iii) the ionic (diffusion) resistance of ions moving in small pores, (iv) The ionic resistance of ions moving through the separator, and (v) the electrolyte resistance [30]. The required electrode properties of supercapacitor electrode material arise from a combination of chemical and physical properties, namely: high conductivity, high surface area range (1 to $> 2000 \text{ m}^2 \text{ g}^{-1}$), good corrosion resistance, high temperature stability, controlled pore structure, process ability and compatibility and relatively low cost. It has been possible to generate high surface area materials exhibiting Faradaic electrochemical as well as electrical double layer type responses. Among the several transition metal oxides and carbon aerogels studied for capacitor response, the only oxide that has been widely researched and known for its superior electrochemical capacitor response to date is the various crystallographic and morphological forms of ruthenium oxide [31]. Unfortunately, the expensive nature of ruthenium has limited the technological viability of this material. Consequently, the field of supercapacitor has not witnessed many advances.

Many chemically deposited metal oxide thin films including ruthenium oxide, iridium oxide, manganese oxide, cobalt oxide, nickel oxide, tin oxide, iron oxide, perovskites, ferrites, etc. have been applied in supercapacitors. The thin film deposition methods involving the growth from solution are called as chemical methods. Here, a fluid surface precursor undergoes a chemical change at a solid surface, leaving a solid layer. In chemical deposition the solutions contain precursor molecules for a variety of elements in the thin film of interest. These methods are inexpensive and enable the synthesis of film materials with complex chemical compositions [32]. Depending on applications, one would prefer thin films which have a special texture, low grain boundary density, or smooth surfaces. The methods usually have low operating temperature. Apart from the obvious advantages in terms of energy saving, the low deposition temperature avoids high temperature effects such as inter diffusion, contamination and dopant redistribution. They offer mysterious morphologies of the thin films which can be easily controlled by preparative parameters. Unlike physical deposition methods, they do not require high quality target and/or substrates nor do they require vacuum at any stage, which is a great advantage if the methods are used for industrial applications. Chemical methods include electrodeposition, chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR), electroless deposition, anodization, spray pyrolysis, liquid phase epitaxy, spin coating, dip drying, etc. This review presents the survey of supercapacitive performance of chemically deposited metal oxide thin film electrode materials. The supercapacitors have exhibited the specific capacitance (Sc) values between 50 and 1100 F g^{-1} , which are quite comparable with bulk electrode values. Therefore, it is likely that these metal oxide thin films will continue to play a major role in supercapacitor technology.

2. Metal Oxides:

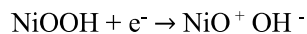
2.1. Cobalt oxide (Co_3O_4) based supercapacitors

Liu et al. [33] reported that Co_3O_4 and CoO_x are for promising materials for supercapacitors due to their intercalative pseudocapacitance properties. Lin et al. [34] obtained a maximum Sc of 291 F g^{-1}

using CoO_x aerogel calcined at 423 K. Srinivasan and Weidner [35] reported Co₃O₄ film used as a positive electrode exhibited capacitor-like behavior. Wang et al. [36] reported Co (OH)₂ electrode exhibits about 280 F g⁻¹ as a single electrode capacitance. The cobalt oxide electrode has been found to have good efficiency and long-term performance and the good corrosion stability [37,38]. The MWNTs/Co₃O₄ composites show high capacitor property, and their best specific capacitance is up to 200.98 F g⁻¹ which is significantly greater than that of pure MWNTs (90.1 F g⁻¹) [65]. A room temperature, simple and low cost SILAR method for the cobalt oxide film on to copper substrate was developed [39]. Cobalt oxide films were deposited from the cationic precursor CoCl₂ complexed with liquor ammonia solution and the H₂O₂ as anionic precursor showed Sc of 165 F g⁻¹ in 1.0 M KOH. Binary hydrous cobaltenickel oxide with an amorphous structure, denoted as a-(Co + Ni) (OH)₂ nH₂O was anodically deposited at + 0.75 V [40]. This deposit with very rough morphology and many small spherical grains aggregated to form the larger oxide particles exhibited Sc of 730 F g⁻¹ in 1 M NaOH. The pseudocapacitance of hydrous oxides mainly came from the electrochemical energy stored by the faradaic redox transitions of interfacial oxyanion species [40, 41]. Similarly, cobalt nickel layered double hydroxides (Co_xNi_{1-x} LDHs) were deposited onto stainless steel electrodes by the potentiostatic deposition method [42]. The Co_xNi_{1-x} LDHs in 1 M KOH electrolyte showed that Co_{0.72}Ni_{0.28} LDHs had the highest specific capacitance value, 2104 F g⁻¹, which is also the highest yet reported value for oxide materials in general. The porous structure with inter-particles spaces increases the electrochemically active sites and therefore, can improve utilization of the LDHs.

2.2. Nickel oxide (NiO) based supercapacitors

Nickel oxide films have been prepared by thermal treatment of electrodeposited Ni(OH)₂ [43-44], sol-gel [46-49] and electrostatic spray deposition [50]. Nickel oxide films synthesized by electrochemical precipitation of Ni(OH)₂ were heat-treated in air [51]. The non-stoichiometric nickel oxide (Ni_{1-x}O) approached the stoichiometric NiO structure with increasing heat-treatment temperature due to the defect healing effect. The defective nature of the nickel oxide could be utilized to improve its specific capacitance. The Sc was from 200 to 278 F g⁻¹ in 1 M KOH within 0.5 V potential windows. The cubic NiO films with different morphologies were prepared by hydrothermal and electrodeposition methods on ITO-coated glass and Ti foil [52]. The Sc of about 148 F g⁻¹ was obtained for the electrodeposited film at 100 mV s⁻¹ scan rate. Using SILAR method, ITO assisted mesoporous and amorphous nickel hydroxide electrodes of 120 m² g⁻¹ surface area (pore-size distribution centered.12 nm) were synthesized [53]. The supercapacitive characteristics in 1.0 M LiCl electrolyte showed the Sc of 85 F g⁻¹. Decreasing trend of supercapacitor value with electrode mass due to the starvation of active sites reacted with ions was observed. Due to the slight phase change from nickel hydroxide to oxide through the intermediate stage of NiOOH, the redox peak was gradually reduced and caused collapse of its intrinsic lattice structure and showed diminution of its capacitance as follows [54];



Liu and Anderson [47] used the sol-gel method to fabricate a porous NiO electrode with a thickness of around 0.4 mm on nickel foil. Srinivasan and Weidner [43] utilized the cathodic precipitation method to fabricate NiO onto gold substrates. Comparative supercapacitor studies on nickel and graphite substrates have been carried out [55]. Thin NiO films were obtained by post-heating of the corresponding precursor films of nickel hydroxide (Ni(OH)₂) cathodically deposited onto graphite and nickel foils. The specific capacitances of the NiO films on nickel foil and graphite were 135, and 195 F g⁻¹, respectively. Electrochemically deposited Nickel and cobalt mixed oxides onto CNT film substrate showed Sc value of 840 F g⁻¹ at the discharge current density of 10 mA cm² in 1.0 M KOH electrolyte [56].

2.3. Indium oxide (In₂O₃) based supercapacitors

Electrodes of different morphologies, i.e. nanospheres (NSs) and nanorods (NRs), made by chemically depositing indium oxide on indium-tin oxide substrates were investigated for their electrochemical supercapacitive properties [57]. The presence of nanosized pores and voids in In₂O₃ electrode of NRs caused increase in redox reaction active sites, and ultimately, inner and outer charges

than that of NSs In_2O_3 electrode. The calculated active sites suggested that the change in surface morphology from NS to NR increased the number of redox reaction sites from 0.02 to 0.3. The Sc values calculated for In_2O_3 electrodes composed of NRs and NSs were 104.9 and 7.6 F g^{-1} , in 1 M Na_2SO_4 , respectively at a constant discharge current density of 8 A/g. Electrodeposition of nanorods of indium oxide of average length of about 250 nm and an average diameter of about 50 nm was carried out by Prasad et al. [58]. The In_2O_3 electrodes in 1 M Na_2SO_3 electrolyte showed Sc of 190 F g^{-1} at a scan rate of 10 mV s^{-1} . There was minimal decrease in Sc for 1000 cycles, indicating stability of In_2O_3 for long-term capacitor applications.

2.4. Bismuth oxide (Bi_2O_3) based supercapacitors

Polycrystalline monoclinic Bi_2O_3 thin films were grown on copper substrates at room temperature by electrodeposition [59]. Though the Bi_2O_3 films are crystalline with a monoclinic crystal structure, they are capable of giving a specific capacitance of 98 F g^{-1} . Typical cyclic voltammograms of Bi_2O_3 electrode deposited on copper substrate in 1 M NaOH electrolyte at scan rate of 100 mV s^{-1} is shown in Fig. 3 [59]. It is seen that the specific and interfacial capacitances decrease from 98 F g^{-1} and 0.022 F cm^2 to 60 F g^{-1} and 0.012 F cm^2 , respectively, as the scan rate is increased from 20 to 200 mV s^{-1} . The decrease in capacitance has been attributed to the presence of inner active sites that cannot sustain the redox transitions completely at higher scan rates.

2.5. Iron oxide (Fe_3O_4) based supercapacitor

An aqueous Fe_3O_4 (magnetite) supercapacitors based on powder form and mixed with carbon black have been studied [64-65]. Large capacitances have been reported in alkali sulfites and sulfate solutions. In particular, the capacitance of the Fe_3O_4 was found to be sensitive to the anion species but not to either alkaline cations or electrolyte $\text{pH} < 11$. These behaviors suggest a capacitance mechanism is different from that of either RuO_2 or MnO_2 . Wang et al. [64] have reported the capacitance mechanisms of an electroplated magnetite thin film electrode in Na_2SO_3 , Na_2SO_4 , and KOH aqueous solutions using electrochemical quartz-crystal microbalance (EQCM) analysis and X-ray photoelectron spectroscopy (XPS), and other electrochemical characterizations [66]. The oxide film exhibited granular morphology with high porosity with an average crystallite size of 12 nm. The Fe_3O_4 electrode exhibited Sc of 170, 25, and 3 F g^{-1} in aqueous 1.0 M Na_2SO_3 , Na_2SO_4 , and KOH, respectively. Strong specific adsorption of the anion species was evidenced in all solutions. Experimental results indicate that, in Na_2SO_3 , the capacitive current of magnetite electrode originate from the combination of electric double layer capacitance (EDLC) and the pseudo capacitance that involves successive reduction of the specifically adsorbed sulfite anions, from SO_3^{-2} through, e.g., S^{2-} , and vice versa. In Na_2SO_4 , the current is due entirely to EDLC. The lowest capacitance of magnetite observed in KOH is attributed to the formation of an insulating layer on the magnetite surface.

2.6. Vanadium oxide (V_2O_5) based supercapacitors

Recently, amorphous vanadium oxides (V_2O_5) have received a lot of attention as electrode materials for supercapacitors in aqueous and organic electrolytes. Lee and Goodenough prepared amorphous V_2O_5 by quenching V_2O_5 powders heated at 1183 K and reported its supercapacitive behavior in KCl aqueous electrolyte with c of 350 F g^{-1} [60]. They proposed that the K^+ ions in the KCl aqueous electrolyte were responsible for the supercapacitive redox reaction of amorphous V_2O_5 . V_2O_5 is also known to have electrochemical redox reactions with Li ions in an organic electrolyte as in lithium secondary batteries [61]. Passerini et al. prepared a sol-gel-derived thin film of V_2O_5 aerogel on a Hastelloy felt substrate and reported a specific energy of 10 Wh/kg with respect to the total mass of a unit cell in LiClO_4 in propylene carbonate [62]. An amorphous and hydrous vanadium oxide ($\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$) thin film of approximate 6-nm thickness was electrochemically prepared onto a carbon nanotube (CNT) film substrate with a three-dimensional porous structure on a nanometer scale for supercapacitor application [63]. From C-V and galvanostatic discharging experiments in an organic electrolyte (LiClO_4 in propylene carbonate), the $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}/\text{CNT}$ film electrode showed Sc of 910 F g^{-1} at a potential scan rate of 10 mV s^{-1} and a

specific capacity of 540 mAh/g at a current density of 10 A/g. The improved Sc of $V_2O_5 \cdot xH_2O$ in the $V_2O_5 \cdot xH_2O/CNT$ film electrode has been attributed to its electrode construction comprising a very thin film of $V_2O_5 \cdot xH_2O$ on the conductive CNT film substrate with a three-dimensional nanoporous structure.

4. Conclusion

(i) Simple chemical methods such as electrodeposition, spray pyrolysis, chemical deposition, spin coating, dip dry etc. have been employed to deposit metal oxide thin films. (ii) For most of the systems, only specific capacitance (Sc) values have been reported and the values of interfacial capacitance, specific energy and specific power are not studied. (iii) In general, stability of electrodes has been reported only for 1000 cycles. (iv) No asymmetric devices formed. (v) Amongst the metal oxide materials, only NiO and Co_3O_4 thin film-based systems have been paid more attention.

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