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Electrode Materials Based on Oxides and Sulfides of Transition Metals and Their Composites: A Review

Qurt-Ul-Ain[*1] and Muhammad Nadeem[2]
[*1]*Department of Basic Sciences, University of Engineering and Technology, Taxila 47050-Pakistan*

Abstract
Supercapacitor, a fascinating electronic device in the field of energy storage possess extraordinary electrochemical characteristics which include enhanced life-cycle stability, fast mechanism of charging and discharging, high capacitance and energy density. In order to bring development and enhancing electrochemical features of supercapacitors, significant attention have been dedicated by researchers in fabrication and novelty of electrode materials. In this regard, composites based on transition metals as electrode materials for supercapacitors have been envisioned. Particularly, transition metals-based oxides, sulfides and their composites along with consequences have been reviewed.

Keywords: *Transition metal, electrochemical, supercapacitor, electrode material, metal oxide, metal sulfides*

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I. INTRODUCTION

Immense focus have been employed in supercapacitors owing to their superior characteristics of excellent cyclic stability, high value of capacitance, high energy density and fast charge-discharge capabilities when compared with traditional capacitors or batteries [1]. For technological advancements, these specific properties significantly influence the capabilities of supercapacitors while applying in any energy storage device. Easy packaging, low-cost maintenance, large heat range and low weight are the characteristics of supercapacitors which give superiority to it over other devices that can store energy [2].

Depending on supercapacitors' charge-discharge phenomenon, following types are allocated: electric-double layer capacitors (EDLCs) whose separation or accumulation of charges takes place at electrode-electrolyte interface for capacitance, and pseudocapacitors (PSC) in which the capacitance is derived as a consequence of redox reaction occurring reversibly at electrode's surface [3]. In EDLCs, active materials having composition of carbon were reported to be employed because they possess excellent life cycle yet are deficient in energy density. While on the other hand, metallic oxides as well as metallic sulfides and conducting polymers have been employed as active material as they possess excellent capacitance but the negative consequence of compromised stability [4-6]. Recently, hybrid supercapacitors have been investigated in which EDLCs as well as pseudocapacitors have been joined together [7].

1.1 The key Parameters for Determining the performance of supercapacitor

For the purpose of determination of efficiency and performance, supercapacitor is tested from its life-cycle, capacitive property, energy as well as power density [8]. For increment in the power as well as density, it is recommended that there must be a significant value of specific capacitance and the range of potential. Range of operating potential is significantly dependent on electrolyte that is to be employed. Electrochemical supercapacitors based on aqueous electrolyte can possess the potential window ranging from 0V to 1V. In case of non-aqueous electrolyte employed in electrochemical supercapacitors, a wider potential can be acquired as compared to aqueous electrolyte. While ionic liquid-based electrolytes are found to be operating at even higher potential window of 3.5V [9].

Properties of electrode materials are also very crucial in order to determine the capacitive behaviour of supercapacitor. Ideal material for electrode should certainly possess following characteristics:

1. Higher specific surface area, as specific capacitance is directly dependent on it.
2. Controlled porosity, as the rate capability and specific capacitance are influenced by it.
3. Higher electronic conductivity, as it is crucial to determine the power density and rate capability.
4. Electroactive sites are mandatory as they permit pseudocapacitance.
5. Higher chemical as well as thermal stability, as cyclic stability is greatly influenced by this factor.

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[1] Qurt-Ul-Ain (q525annie@gmail.com)

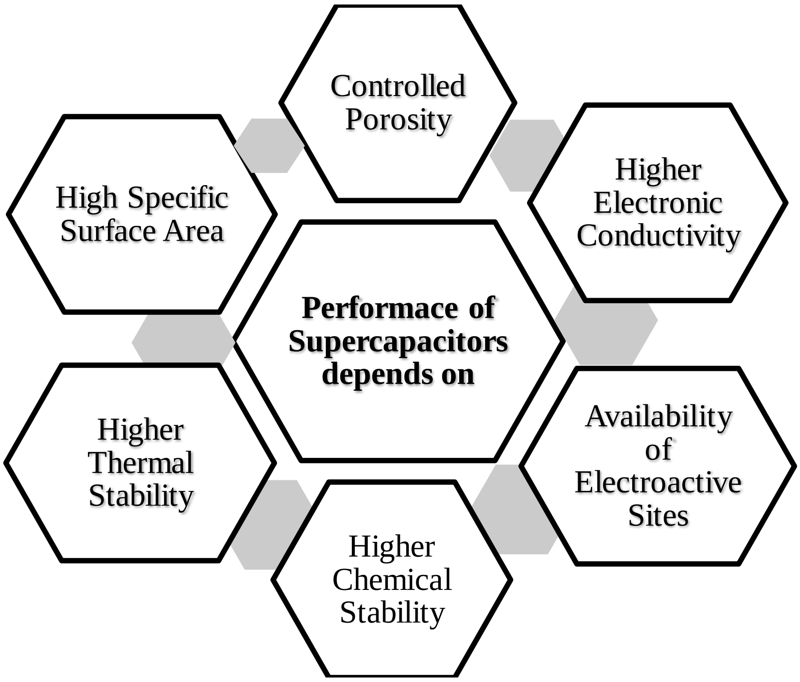

Figure 1: key Parameters for Determining the Performance of a Supercapacitor

II. TRANSITION MATEL-BASED ELECTRODE MATERIALS

Due to the possession of unique and extraordinary physical as well as chemical properties, various nanomaterials have been found to be an appropriate candidate for their applicability in fields of energy storage e.g. supercapacitors [10]. In present review, electrode materials based on oxides and sulfides of transition metals and their composites are comprehensively discussed. In order to meet the technological advancement, their properties, modification and developmental works are also reviewed.

2.1 Metallic Oxides-Based Electrodes

Metallic oxide are to be utilized for various applications of energy storage, specifically as materials for fabrication of electrodes of supercapacitors having characteristics of environmental friendly, cost-effective as well as highly capacitive behaviour [11-17]. While fabricating metallic oxides, various strategies e.g., formation of nanoarchitectures, joining composites of oxides with numerous oxidation states and more than one metallic oxide composites make them capable for application in electrochemical storage devices partaking elevated energy and power density as advanced electrode material.

Various oxides metals e.g., Mn, Ni, Co, Fe**,** etc. having pseudocapacitive characteristic have been extensively studied owing to their superior characteristics of cost effectiveness, reversible faradaic redox reaction and higher theoretical capacitances and thus they get excel in the perspective of specific capacitance over carbon-based materials [14, 18-29]. There are some more transition metal oxides in which faradaic behaviour is observed in their charge storage mechanism and they are: RuO_2, Co_3O_4, Fe_3O_4, NiO, MnO_2, IrO2, CuO and V_2O_5 [30, 31].

2.1.1 Binary Transition Metal Oxides-based Electrodes

Despite of exhibiting outstanding electrochemical performance, metal oxides are reported to be inferior in electrical conductivity and rate capability. Multiple studies reveal that in various bimetallic oxides, good electrical conductivity, higher thermal and mechanical stability together with active sites aimed at redox activity lead to higher specific capacitance of them when compared to their corresponding single metallic oxides [32-40]. Similarly, binary metallic oxides like, $NiCo_2O_4$ expose much developed electrical conduction than that of the oxides of cobalt and nickel. In case of $FeCo_2O_4$, it also exhibits extraordinary electrochemical activity as both cobalt and iron exhibit good electrochemical performance and this delivers extra functioning sites for redox activity than their corresponding single counterparts [22].

2.1.2 Mixed-Transition Metal Oxides-Based Electrodes

In order to achieve high performance of supercapacitors, another idea that is gaining significant attention is that of the fabrication of electrodes based on mixed metal oxides by incorporating a number of functionalities in organic framework of metals (MOF) and developing high surface area and some of them are: as $ZnO@ZnCo_2O_4$, CuO@NiO, Fe_2O_3/Co_3O_4, $NiFe_2O_4/Fe_2O_3$, $Fe_2O_3@TiO_2$, $Co_3O_4/NiCo_2O_4$, , $Co_3O_4/ZnFe_2O_4$, $Cu/Cu_2O@TiO_2$, $ZnO/ZnFe_2O_4$, NiO@ZnO, $ZnO@Co_3O_4$, $Fe_2O_3/NiCo_2O_4$, and CuO/Cu_2O [41-55].

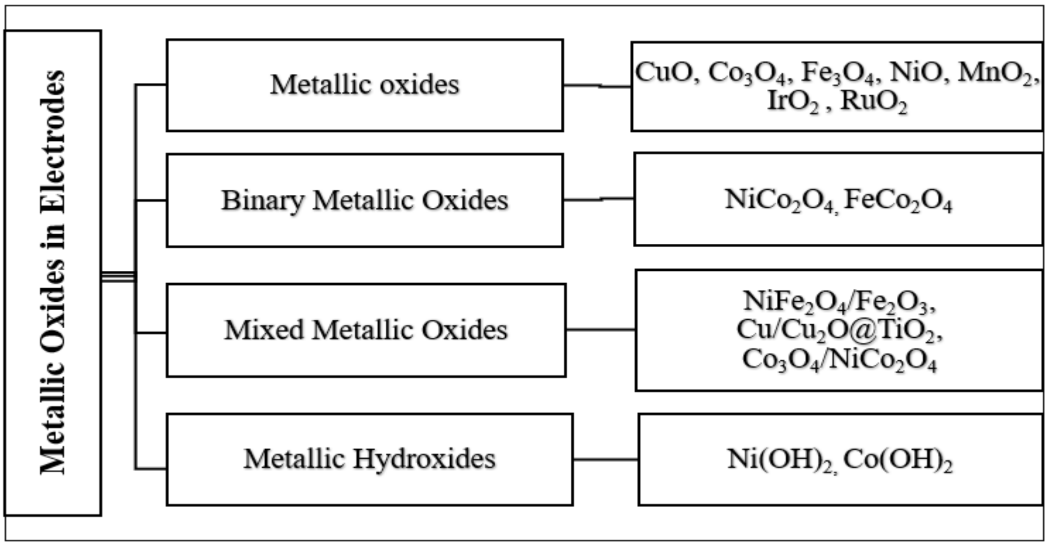

Figure 2: Numerous Electrode Materials of Metallic Oxides

2.1.3 Metallic Hydroxides-based Electrodes

Further, transition metal hydroxides-based electrodes like $Ni(OH)_2$, $Co(OH)_2$ etc. are likewise playing significant role in enhancing the capacitance of supercapacitors, as in between their layers, there is enough space, and they also impart their role in redox reactions. Although higher charge storage is offered by transition metal hydroxides as compared to their corresponding metal oxides, but they still have lesser electronic conductivity as compared to their corresponding oxides. As compared to their corresponding oxides, lower structure stability is exhibited by transition metal hydroxides, as a consequence of which they offer decreased cycling stability. However, multiple strategies are found applicable in order to minimize this limitation and enhance the cycling performance such as layered engineering of transition metal hydroxides by utilizing the cation and anion doping process [56].

Despite of exhibiting satisfactory electrochemical characteristics, transition metal oxides still possess limited conductivity and thus offering decreased rate capability. So, practically capacitances of metal oxides differ much from theoretical assumptions because they are intrinsically deficient in electronic and ionic conductivities[57]. In order to adjust the nanostructure of metal oxides, some significant strategies are employed which include, incorporation of metallic oxides into substrate which are conducting, fixing of metals with the intention of boosting the conductivity plus redox reaction and linking transition metal oxides composites with various oxidation states etc. [15, 56, 58-60].

2.2 Transition Metal Sulfide-based Electrode Materials

Other potential materials utilized for fabrication of electrodes for energy storage applications are transition meta sulfides and they are CoS, MoS, FeS, NiS, MnS etc., and they own extraordinary electrochemical characteristics [61]. Transition metal sulfides are found to have much superior electrochemical properties that that of electrochemical characteristics of transition metal oxides and these characteristics are attributed to the existence of sulfur in transition metal sulfides instead of oxygen atom. Electron transfer process is much easier and facilitated by inferior electronegativity in sulfur atom in structure of sulfides of metals. Hence, more flexibility is introduced in the fabrication of nanomaterials due to the replacement of oxygen with sulfur [62].

Supercapacitors besides Lithium-ion batteries are the arenas of research in which transition metal sulfides consume tremendous concentration be indebted to distinctive characteristics of them for instance, unique optical along with electric properties and these properties are significantly enhanced when nanocomposite structures are prepared by combining other materials [63]. Excellent electrical conductivity, good redox activity, significantly high specific capacitance, low electronegativity of sulfur in them and unique structure of crystal lattice are the distinctive properties due to which transition metal sulfides exhibit excellent electrochemical characteristics and are emerging electrode materials [64]. These extraordinary electrochemical features of transition metal sulfides generally belong to their particular structure with outstanding morphology of surface in terms of uniqueness in shapes like nanowires, nanorods, hierarchical etc. Extensively studied pseudocapacitive materials called transition metal sulfides also possess the efficiency of supplying high energy density [65-71].

2.2.1 Binary Metallic Sulfides as Materials for Electrodes along with their Composites

From corresponding metallic oxide or metal hydroxide precursors, a number of metal sulfides have been reproduced hydrothermally processed through bartering anion, who follows Kirkendall mechanism in which effective growth of tunable morphologies like nanotubes, nanowires, nanosheets and nanoparticles [14, 72-76]. NiCoS nanosheets arrays arranged over carbon cloth is reported by Liu T et. al. as electrodes for supercapacitor application. Uniqueness in structure of this composite electrode material displays grander electrochemical activity attributable to accessibility of plentiful dynamic sites for reaction.

Binary transition metal sulfides involve their various composites along with various other materials like Oxides, sulfides and hydroxides etc. [77-81]. The sulfides, oxides and hydroxide which contribute towards composition of a nanocomposite with transition metal sulfides provide supplementary functioning sites for electrochemical redox reactivity so as for the expansion of rate performance and capacity. For the purpose of electrochemical energy storage, a lot of exertions have stood employed concerning the fabrication of mixtures based on binary metallic sulfides [82]. MoO2/MoS2, SnS2–SnO2, NiCo2S4@NiO, SnNi2S4, ZnS/MnS, CuS/MnS and CuWS/Ni are some more examples of synthesized materials founded on binary metallic sulfides composites intended for electrode material [83-90].

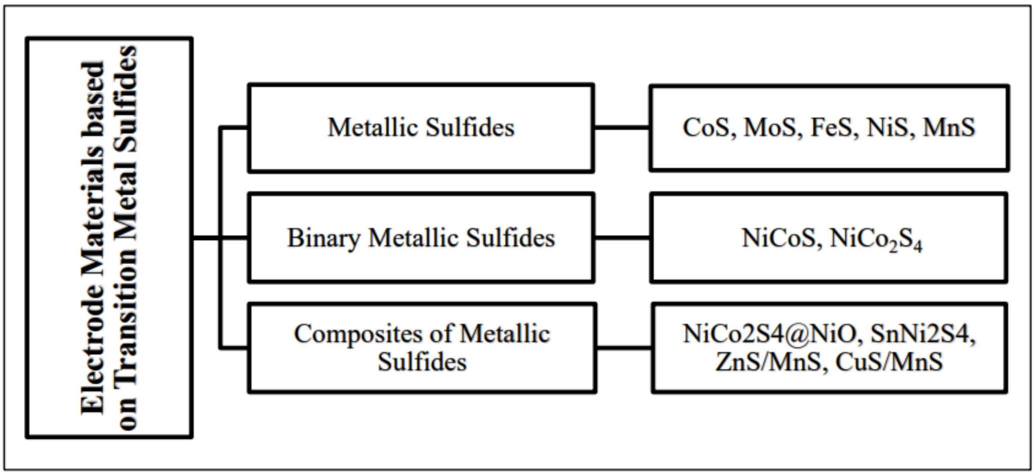

Figure 3: Metallic Sulfides as Materials for Electrode

Some major drawbacks of metal sulfides include the inadequate interlayer spacing in the encrusted material of transition metal sulfides that obstructs the transference of charge and applies constraints in the marketable application. Synthesizing composite of metal sulfides with Mxene and metal organic framework is great idea in order to minimize this drawback and enhance the interlayer spacing. Narrow band gap of transition metal sulfides and performing faradaic redox reaction while charging and discharging process results in the low potential window, short life cycle stability and energy density. This issue can also be addressed by utilizing anions with greater ionic polarizability so that metal sulfides may exhibit faster ionic diffusivity [90].

III. CONCLUSION

In this review, the oxides and sulfides of numerous metals applied in electrodes fabrication and their variation in application of supercapacitor have been comprehensively discussed. Electrode constituents built on metallic oxides in addition to their consequences have been reviewed. They were found as auspicious electrode resources owed to their possessions of cost effectiveness, reversible faradaic redox reaction and high theoretical capacitance, and specifically in terms of capacitance, they are preferred over carbon-based electrode materials. Despite of all these characteristics, as they lack in electrical conductivity intrinsically, still there application and utilization for commercial purposes are limited. To overcome this hurdle, binary metallic oxides, mixed-metallic oxides plus metallic hydroxides-based nanomaterials and various nanocomposites of them have also been investigated by many researchers and some of them are reviewed here. Transition metallic sulfides also were studied generally and explored for electrodes fabrication intended for utilization as supercapacitor applications. Existence of sulfur and its low electronegativity in metal sulfides makes them superior over metal oxides-based electrode materials as metal sulfides possess some distinctive characteristics like good electrical conductivity, excellent redox activity, significantly high specific capacitance and unique structure of crystal lattice. Binary metal sulfides and their composites along with characteristics have also been reviewed.

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