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A Concise Review Electrochemical Supercapacitors: Electrode Materials and Device Fabrication

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Electrochemical energy storage devices are considered as the propitious candidates to meet the energy needs of the future generations. Supercapacitor is one among which has its own unique properties such as long cycle life, rate capability, high capacitance and low cost. Due to these advantages, they are also investigated for the future power applications. Since electrode material plays a vital role in the performance of supercapacitor, there has been an immense attention paid by researchers to explore new materials. Furthermore, many investigations are also carried out to fabricate capacitor devices in various configurations to improve the energy and power densities. In this paper, we give a brief outline of electrode materials for supercapacitor and recent advancements in the device fabrication.

Keywords: *Energy Storage, upercapacitor, Electrode Materials.*

1.0 INTRODUCTION

Energy is ubiquitous in our lives and is so common that we seldom even think about it. Energy Consumption is an absolutely necessary component for the industrial society. Due to the growing energy requirement, there is a great demand for energy. Till date, fossil fuels have been largely used for the energy demands. But with limited resources, there is an urge to develop alternate energy sources [1]. Nowadays, creating energy through various means such as solar, wind, biomass, hydro have become trivial and the new technologies would address the challenges in energy sector. Simultaneously, the storage of energy is also an important concern. So, many efforts have been devoted to develop the electrochemical energy storage devices and integrating them in innumerable applications. One among the few storage devices is the supercapacitor which also called as an ultracapacitor [2].

A supercapacitor is a high capacity electrochemical capacitor that bridge the gap between electrolytic capacitors and rechargeable batteries. Being an alternative to traditional batteries, the supercapacitor has its own benefits such as high power density, long cycle life, flexible packaging, low weight, low maintenance, reliability and improved safety [3]. Although its energy density is lower than batteries it has very high power capability which can bridge the short time duration between a power failure and the startup of backup power generations. Since the electrode material is the most vital component in a supercapacitor, their electrochemical performance strongly depend on surface area, conductivity and permeability of electrolyte solution. Many researchers have put their effort to increase the energy density to an extent to where the energy density of supercapacitors comparable with batteries [4]. This paper describes about the effective electrode materials and electrochemical cell performance of supercapacitor.

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2.0 CLASSIFICATION OF SUPERCAPACITOR

Supercapacitors can be classified into three types: Electrochemical double-layer capacitors, pseudocapacitors, and hybrid capacitors. Each type is characterized by its unique mechanism for storing charge. The energy storage process is through non- Faradic, Faradic and a combination of the both respectively. These three types and their subclasses are distinguished by electrode materials [5].

2.1 Non-Faradic Materials:

Electrochemical double-layer capacitors (EDLC) are said to be non-faradic because it stores charge electrostatically and there is no transfer of charge between electrode and electrolyte. When voltage is applied, accumulation of charge takes place at the surface of electrode. This storage mechanism allows good cyclic stability, better power performance and non-toxicity. Generally, EDLCs consist of carbon-based materials such as carbon nanotubes (CNT), activated carbon (AC), carbon aerogel, and carbon nanofibers (CNF) etc. Leng et al discussed the high performance bio-based activated carbon (BAC) via a novel combination of chemical and physical activation processes using coconut shells as a precursor [6]. It exhibited a high specific capacitance of 337 Fg_{-1} and retained a specific capacitance of 331 Fg_{-1} after 10,000 cycles (98% capacitance retention) at a current density of 0.5 Ag_{-1} in 6 M KOH. Pech et al integrated microsupercapacitor nanoparticles inside a micro device with a high surface-to-volume ratio, without the use of organic binders and polymer separators shows superior performance because of the ease with which ions can access the active material [7]. Zheng et al investigated a hierarchical porous water hyacinth-derived carbon as electrode material for supercapacitor [8]. It exhibited a specific capacitance of 344 Fg_{-1} at a current density of 0.5 Ag_{-1} and also a good rate performance even at a current density of 30 Ag_{-1}, and good cycle stability. Subramani et al reported activated carbon derived from orange peel for fabrication of supercapacitor [9]. The activated nano-porous carbon exhibited a high specific surface area 2160 m_2 g_{-1} with the uniform meso and micropores.

2.2 Faradic Materials

Pseudocapacitors are considered to be faradic in nature because it involves the transfer of charge between electrode and electrolyte. When voltage is applied the redox reaction (i.e Oxidation and reduction) takes place on the electrode material. This charge storage mechanism will aid to achieve greater specific capacitance and energy density when compared to EDLC (Non-Faradic material). Metal oxides, metal hydroxides, polymers and their composites have been examined as electrode material for pseudocapacitors. Sim *et al*. reported the synthesis of NiMn-Layered double hydroxide nanoplatelets by a reverse micelle method and it showed a specific capacitance of 881 Fg_{-1} at 0.5 Ag_{-1} in 1 M KOH solution [10]. Liu et al suggested that cation leaching effect should be seriously considered in the development of new perovskite oxides as anion-intercalation-type electrodes for supercapacitors [11]. Jiang et al reviewed recent progress of metal oxide-based hybrid nanostructure film arrays used as electrode materials for enhancement of supercapacitor performance [12].

2.3 Hybrid Materials

Hybrid capacitors attempt to exploit the relative advantages and mitigate the relative disadvantages of EDLCs and pseudocapacitors to realize better performance. Utilizing both Faradaic and non- Faradaic processes to store charge, hybrid capacitors have achieved energy and power densities greater than EDLCs without sacrificing both cycling stability and affordability that have limited the success of pseudocapacitors. Research has focused on three different types of hybrid capacitors distinguished by their electrode configuration: composite, asymmetric, and battery-type. Jiang et al reported the advantages of the VACNTs/ GF substrate in the hybrid electrode with V_2O_5 embedded among the VA-CNT interstitials for high-performance flexible energy storage devices [13]. Chen et al discussed the in-situ formation of a carbon fiber@Ni_3S_2 non-woven electrode which shows ultrahigh volume/ area capacitance [14].

3.0 SUPERCAPACITOR PERFORMANCE

3.1 Half Cell Performance:

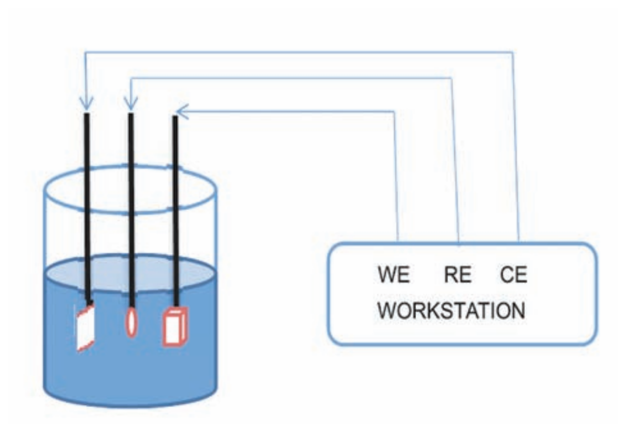

FIG 1 SCHEMATIC OF HALF CELL

The half-cell performance of supercapacitor is generally denoted by three electrode configuration to measure its electrochemical behavior. Figure 1 shows the schematic view of three electrode configuration. It consists of working electrode (WE), reference electrode (RE), counter electrode (CE) and electrolyte. Active materials are coated on to the working electrode. Standard Calomel electrode (SCE), Ag/AgCl Electrode, Hg/HgO Electrode are often used as reference electrode and platinum as counter electrode. Mostly aqueous solution is used as electrolyte.

The electrochemical performance of supercapacitor is evaluated by cyclic voltammetry (CV), galvanostatic charge- discharge (CD) and electrochemical impedance spectroscopy (EIS). Through these methods various parameter such as specific capacitance, cycle life, columbic efficiency and impedance spectroscopy can be calculated [15,16].

Form charge discharge studies, the specific capacitance can be calculated from the formula:

$C = I*t/\Delta V*m$ [17]

Where, C is specific capacitance (Fg^{-1}), I is current (A), t is discharge time(s), ΔV is potential window (V) and m is active mass (g). The symmetry of the charge-discharge curves will reflect in the reversibility of active materials. When the symmetry curve is more proper, the reversibility is better for active materials [18].

The specific capacitance was calculated from the CV curves by using the following formula:

$C = Q/V*m$ [19]

Where, C is specific capacitance (Fg^{-1}), Q is charge (coulomb), v is potential window (V) and m is active mass (g). From the shape of CV curves, the performance of supercapacitor will be reflected. If the shape is more close to a rectangle, then it exhibits EDLC behavior (or) else if there is a redox peak, then pseudocapacitor behavior is seen. In addition to this, cycle life can also be evaluated from these methods.

3.2 Full Cell Performance:

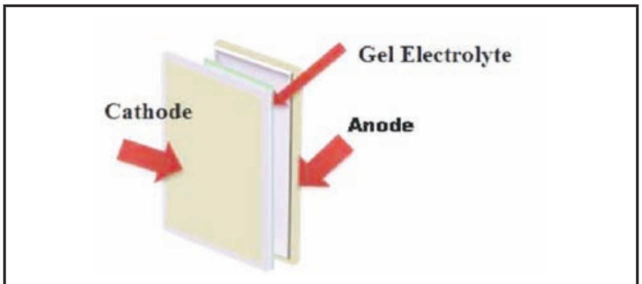

FIG 2 SCHEMATIC OF SUPERCAPACITOR DEVICE

The full-cell performance of supercapacitor is generally denoted by two electrode configuration. Figure 2 shows the schematic view of two electrode configuration. Both the electrodes were coated with the active materials which are separated by a fibrous membrane sheet which was soaked in electrolyte solution or a polymer gel is mixed with the electrolyte solution to make a fine membrane film. Based on the type of active materials used in the device a capacitor device can be fabricated into three types [20].

(1) Symmetric Supercapacitor

(2) Asymmetric Supercapacitor

(3) Battery-type supercapacitor

In symmetric supercapacitor, researchers use same active material for both anode and cathode electrodes. Recently, Bai et al., reported that symmetric supercapacitor possess an maximum energy density of 8.9 Wh/kg and maximum power density of 10,000 W/kg for pumpkin-derived porous carbon for supercapacitors with high performance [21]. Similarly, Mo et al. reported that the maximum energy density of 11.39 Wh/kg was achieved for activated carbon derived from nitrogen-rich watermelon rind for high performance supercapacitors [22]. Asymmetric supercapacitors use different materials i.e metals/metal oxides, polymer and composite material as anode (positive electrode) which shows pseudo behavior and carbon based materials as cathode (negative electrode) which exhibits EDLC behavior [23]. Most preferably solid state or gel type electrolyte will be used to avoid leakage. Karthik kiran et.al reported an asymmetric flexible supercapacitor using CoCr-layered double hydroxide and reduced graphene-oxide with a wide potential window of 1.6 V delivering a power density of 4860 W kg^{-1} [24]. Liu et.al reported an asymmetric supercapacitor having an energy density of 17.9 $Whkg^{-1}$ using Co_3O_4 nanowires and carbon aerogel [25]. Battery-type hybrid supercapacitor has one electrode made from carbon material to maximize the power density and other electrode is battery-type material which is made by sandwiching materials taken from a capacitor (e.g porous carbon materials) and the other from a battery type material hybrid (e.g. metal oxides/hydroxides). Padmini et.al reported a hybrid energy storage device based on rGO anchored with NiMn-LDH with an energy density of 22.5 W h kg^{-1} [26].

4.0 CONCLUSION:

With the advent of supercapacitors a new promising solution for alternative energy storage has been developed. A new class of electrode materials and different methods emerged for the development of electrochemical energy storage devices. By choosing a proper combination of electrode material and appropriate fabrication method, one can enhance energy density, cycle life, power density of a supercapacitor device. Simultaneously, the cost also should be taken into consideration for commercialization of a practical supercapacitor. In the near future, with new advancements in materials technology and cost-effective fabrication methods supercapacitors might become a real option to accommodate the battery in terms of enhanced power and energy densities.

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