Materia, Ciencia y Nanociencia

www.uv.mx/veracruz/microna/mcyn ISSN: en trámite
Revista Materia, Ciencia y Nanociencia | Vol. 2, No.1, Junio 2019

MoS_2-TiO_2-GRAPHENE OXIDE COMPOSITES FOR SUPERCAPACITOR APPLICATION

COMPOSITOS DE OXIDO DE GRAFENO MoS_2-TiO_2 PARA APLICACIÓN EN SUPERCAPACITORES

Gnanaseelan Natarajan[1], Duraisamy Eazhumalai[2], Elumalai Perumal[2], Sathish-Kumar Kamaraj[3], Felipe Caballero-Briones[1]*

[1]Instituto Politécnico Nacional, Materiales para Energía, Salud y Medioambiente (GESMAT), CICATA Altamira, Km 14.5 Carretera Tampico-Puerto Industrial Altamira, 89600 Altamira Tamaulipas, México.

[2]Department of Green Energy Technology, Madanjeet School of Green Energy Technologies, Pondicherry University, Puducherry 605014, India.

[3]Tecnológico Nacional de México, Instituto Tecnológico El Llano Km. 18 Carr. Aguascalientes-San Luis Potosí, 20330 El Llano, Aguascalientes, México.

Email: fcaballero@ipn.mx

ABSTRACT

The coming decades would witness tremendous growth of electrical transportation for various reasons from combating global warming to sustainable technological advancements. Supercapacitors are considered as a viable safer alternative to conventional batteries for electric buses because of its unique qualities such as high power density and rapid charge-discharge behavior. Electrochemical double-layer supercapacitor (EDLSC) devices store charge by adsorption of electrolyte ions onto the surface of electrode materials. The absence of diffusion-controlled redox reactions in these devices allows to fast response to changes in potential and leads to high power density. Graphene has unique 2D structure and exotic intrinsic properties such as excellent electrical conductivity and large surface area. Superior chemical stability and broad electrochemical window make graphene-based composites attractive electrode materials for supercapacitors. The aim of our work was to develop novel graphene oxide based composite for supercapacitor applications. The concepts of supercapacitors and the techniques used for study them are discussed

Key words: *EDLC, Graphene oxide, 2D materials, Supercapacitor.*

Fecha de aceptación: Mayo 30, 2019.

RESUMEN

Las próximas décadas serán testigo del enorme crecimiento del transporte eléctrico por varias razones, desde la lucha contra el calentamiento global a los avances tecnológicos sostenibles. Se considera que los supercapacitores son alternativas viables más seguras a los autobuses eléctricos debido a sus cualidades únicas, como la alta densidad de potencia y el rápido comportamiento de descarga y carga. Los dispositivos supercapacitores electroquímicos de doble capa (EDLSC) almacenan la carga por adsorción de iones de electrólitos en la superficie de los materiales de los electrodos. La ausencia de reacciones redox controladas por difusión en estos dispositivos permite una respuesta rápida a los cambios en el potencial y conduce a una alta densidad de potencia. El grafeno tiene una estructura 2D única y exóticas propiedades intrínsecas, como una excelente conductividad eléctrica y una gran área de superficie. La estabilidad química superior y la amplia ventana electroquímica hacen que los compuestos a base de grafeno sean materiales de electrodos atractivos para supercondensadores. El objetivo de nuestro trabajo fue desarrollar un nuevo compuesto a base de óxido de grafeno para aplicaciones de supercapacitores. Se discuten los conceptos de supercapacitores y las técnicas utilizadas para el estudio.

Palabras clave: *EDLC, materiales 2D, óxido de grafeno, Supercapacitores.*

INTRODUCCIÓN

The growing energy demand and the reduction in available fossil energy sources make us to rely more on the renewable energy resources. Enormous research has been devoted to explore new ways to harness the naturally available energy and its efficient way of storing it. For example, solar energy is an alternative, renewable and abundant source and its conversion to chemical and electrochemical energy has been gaining lot of interest to meet the growing global energy demand.

On the other hand, communication and information technology have been witnessing a tremendous growth in this century. This development has resulted in many portable devices such as laptops, mobile phones, and other gadgets. The active functioning of these portable devices mainly depends on the power storage devices. Li-ion batteries have proved their immense role in realizing these smart portable devices. In addition, the application of electrochemical energy storage devices to transportation is widening due to following reasons viz., depleting petroleum resources, skyrocketing oil prices and concerns on global climate change. Moreover, supercapacitors will be boon for wind energy technology to maintain the stability of the grid with synchronized voltage and frequency. Li-ion battery will be suitable for photovoltaic power plant.

Supercapacitors have high power density, long cycle stability and fast charging-discharging capability whereas Li-ion battery has high energy density so that energy can be retained for longer durations. Supercapacitors exhibit long life with more than 100000 cycles. Supercapacitor has more than ten times of power density when compared to Li-ion battery, although the specific energy of commercially available supercapacitors is less than 10 Wh/kg whereas that of batteries is in range of 70-100 Wh/Kg [1].

Capacitor is passive electronic device consisting of two metal plates separated by a dielectric medium. The applications of the electrochemical capacitors are memory back-up, electric and hybrid vehicles, power quality improvement for the application of electric power system [2-3]. In 1957, General Electric first demonstrated the supercapacitors and patented it [4]. Conventional capacitors consist of conducting electrodes that are separated by a dielectric medium. When potential is applied between the electrodes, opposite charges are accumulated on it and producing the electric field [5]. This leads to the storage of the energy. Capacitance is given by the formula:

$$C = \frac{Q}{V} \tag{1}$$

where C = capacitance, Q = charge and V = voltage. C is also expressed by following equation:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{D} \tag{2}$$

where , $\mathcal{E}o$ = dielectric constant (or permittivity") of free space, $\mathcal{E}_r$ = dielectric constant of the insulating material between the electrodes. The energy stored in the capacitor is given by following formula

$$E = \frac{1}{2} C V^2 \tag{3}$$

Supercapacitors also work with same principle of conventional electrode, but it incorporates the following differences:

1. Electrode materials have a much higher surface area (A).

2. The dielectric material is thinner, which decreases the distance between the two electrodes (D).

From equations 2 and 3, it is easily understood how a supercapacitor has more power density and having more energy density when compared to conventional capacitor. Schematic diagrams of both types of capacitors are shown in Figures 1 and 2.

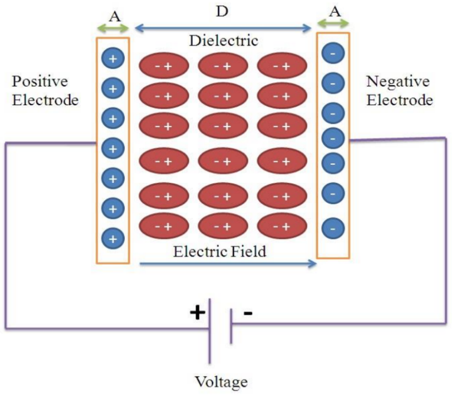

Figure 1. *Schematic diagram of conventional capacitor.*

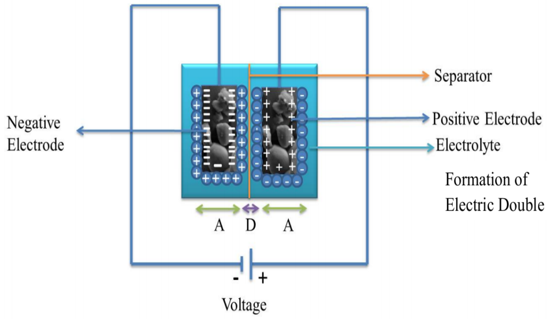

Figure 2. *Schematic diagram of a supercapacitor.*

The types of electrochemical capacitors are

1. Electric double layer capacitors (EDLC)
2. Pseudocapacitors
3. Hybrid Capacitors

EDLC mostly use carbon materials which stores energy at the pores. Pseudocapacitive electrodes consist of metal oxides and hydroxides, and conductive polymers and use fast and reversible chemical reactions for energy storage. Hybrid capacitors have both functionalities.

Electric Double Layer Capacitor (EDLC), as its name suggests it stores energy by formation of electric double layer as shown in the Figure 2. As voltage is applied between the electrodes, oppositely charged ions in the electrolyte diffuse through the pores of the electrode, leading to the formation of an electrical double layer, storing the charge. The higher surface area and very thin dielectric medium contributes to more energy storage compared to a conventional capacitor, as shown in Figure 2.

EDLC stores energy electrostatically. It does not involve any chemical reaction or charge transfer and non-faradaic reactions are primary reason for EDLC which is highly reversible and stable over more than 10^6 cycles. Its performance could also be altered by using different electrolytes. The capacitance for acidic electrolyte is higher than the basic electrolyte. Carbon materials are generally used as electrode material for EDLC.

In the present work, molybdenum sulfide–titanium oxide–graphene oxide composite was synthesized for the application in EDLC supercapacitors. MoS_2 has layered structure in which Mo is sandwiched between two layers of sulfur that could store more charges into it. TiO_2 is chemically stable compound and offers solvated ion accessible surface area. The addition of MoS_2 with TiO_2 would improve textural and structural properties. The performance can be enhanced by coupling the composite with an electron accepting such as graphene. The addition of graphene oxide to the composite further improves the composite by rendering high surface area and mechanical stability [6].

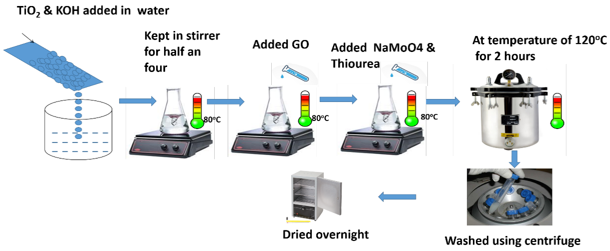

Figure 3. *Schematic diagram to synthesis* MoS_2-TiO_2-*Graphene Oxide.*

As shown in Figure 3, a solution was made of KOH and TiO_2 nanoparticles in deionized water. Then the solution is kept in the hot plate magnetic stirrer at 90ºC. Another solution was made by adding graphene oxide in water and kept under constant stirring for an hour. Finally, yet an another solution was made by a mixture of $Na_2MoO_4.6H_2O$ and water and out under magnetic stirring for one hour. Finally, the mixture was transferred to autoclave and kept overnight.

The performance of a supercapacitor material is tested by electrochemical methods. Electrochemistry deals with the flow of electrical charge corresponding to the chemical changes during oxidation and reduction processes when a potential is applied to the electrode of the material under test. A typical electrochemical set-up consists of an anode, a cathode and an electrolyte. Anode is terminal, where the current flows in from outside in electrochemical setup. Cathode is terminal, where current flows outside. Electrolyte is electrically conducting solution, which consists of positive and negative ions. As already discussed, supercapacitors are electrochemical devices, which can be studied by cyclic voltammetry, i.e. assessing the current magnitude during a cyclic potential excursion. Figure4 shows cyclic voltammetry measurement for MTG sample. Both anode and cathode electrodes were coated with MTG sample and 0.5 M of KOH was used as electrolyte.

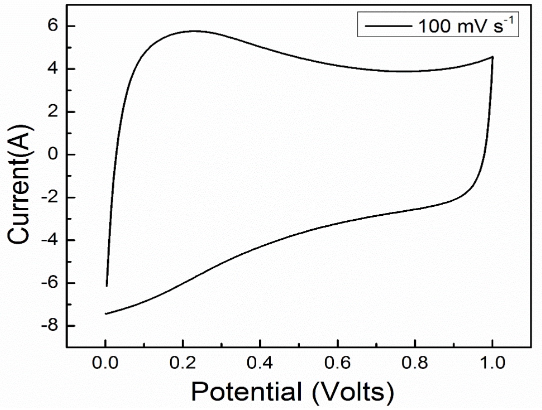

Figura 4. *Cyclic voltammetry of MTG.*

In Figure 4, x-axis represents the applied potential and y-axis is the resulting current obtained during the potential excursion. The applied potential was varied linearly at scan rate of 100 mV per second. The current increased steeply when the potential excursion began at 0V up to positive values. Then the current value stay almost constant up to 1 V, when it decreased abruptly to keep another constant value down to 0 V. Since the curve do not display any peak, it is inferred that the material do not undergo any oxidation and reduction process. *i.e.* faradaic processes. The current increased as the electrode is stored into the electrodes in the positive potential direction, decreased as the electrode discharges and stay at a negative value when the charge is stored in the opposite electrode. From the behavior, it can be concluded that MTG composite material exhibits a typical EDLC behavior. Figure 5 shows the charge-discharge characteristics of the material. In this measurement, a current is imposed to the electrode to force the charge accumulation and therefore, the building of a potential.

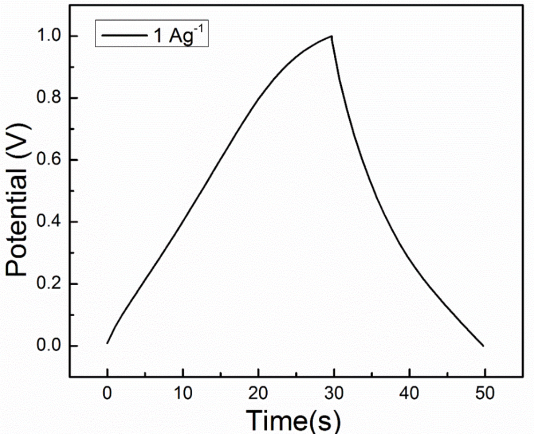

Figure 5. *Charge-discharge profile for MTG composite.*

The upward curve, where the voltage is increasing with the time, indicates the charging of the supercapacitor; the second half of the plot, when the voltage decreases, represents the discharging of the supercapacitor. The specific capacity of supercapacitor can be calculated by using the following formula, deriving values from Figure 5.

$$C_{SP} = \frac{I \times \Delta t}{\Delta V \times m} \tag{4}$$

Where I is the discharge current (A), Δt is the discharge time (s), ΔV is the potential window, and m is the mass (g) of the active material. The specific capacity of MTG composite was 90 F/g. At a given current value (I), the increase rate in the voltage is related with the power density of the supercapacitor, i.e. the amount of accumulated charge per time unit. This symmetrical behavior of the charge-discharge curve demonstrates that the MTG material has a supercapacitor behavior that could deliver high power in a short period of time, *i.e.* a high power density.

CONCLUSIONS

In this paper, the principles of energy storage devices, and particularly supercapacitors were discussed. The characteristics of EDLS supercapacitors were described, in order to understand the properties of MoS_2–TiO_2-graphene (MTG) composites synthesized by hydrothermal methods. The specific capacitance as well of the charge-discharge behavior of the MTG in the presence of a 0.1 KOH electrolyte were determined by electrochemical methods. The principles of the measurements and the obtained curves were discussed for a deep understanding of the materials.

Acknowledgements

This work was partially financed by SIP-IPN 20194931 project. GN acknowledges BEIFI and CONACYT grants.

REFERENCES

[1] J.R. Miller and A.F. Burke, Electrochemical capacitors: Challenges and opportunities for real-world applications, Electrochem. Soc. Interface, Vol. 17, pp. 53-57, 2008.

[2] P. Jampani, A. Manivannan and P. N. Kumta, Advancing the supercapacitors technology frontier for improving power quality, Electrochem. Soc. Interface, Vol. 19, pp. 57-61, 2010.

[3] A.K. Shukla, A. Banerjee, M. K. Ravikumar and A. Jalajakshi, Electrochemical capacitors: Technical challenges and prognosis for future markets, Electrochim. Acta, Vol.84, pp. 165– 173, 2012.

[4] Yan Wang, Zhiqiang Shi,Yi Huang, Yanfeng Ma, Chengyang Wang Mingming Chen and Yongsheng Chen , Supercapacitor devices based on graphene materials J. Phys. Chem. C, Vol. 113, pp. 13103–13107, 2009.

[5] M. S. Halper and J. C. Ellenbogen Supercapacitors: A brief overview, 2013.

[6] Yang, Xixian, Hongyu Huang, Mitsuhiro Kubota, Zhaohong He, Noriyuki Kobayashi, Xiaosong Zhou, Bei Jin, and Jin Luo, Synergetic effect of MoS_2 and g-C_3N_4 as cocatalysts for enhanced photocatalytic H_2 production activity of TiO_2, Materials Research Bulletin, Vol 76, pp. 79–84, 2016.