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COBALT DOPED MANGANESE OXIDE- CONDUCTING POLYMER NANOCOMPOSITE AND ITS PROPERTIES

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ABSTRACT :

   The energy requirement of earlier decades was fulfilled by conventional energy resources especially fossil fuels like coal and petroleum products. The demand for energy sources is going on increasing due to increased usage of automobile, electrical, and electronic appliances of both domestics and industries. In order to develop and find alternates to switch over from non- renewable to renewable at the same time pollution free energy sources, Scientists are still doing research towards the development of new energy producing materials. In line of this kind of research, we

made an attempt to develop new class of materials for the same purpose. Supercapacitors are the future energy storage devices. In our present study we have developed nanocomposite having capacitance properties and it will be continued in our future research perspectives.
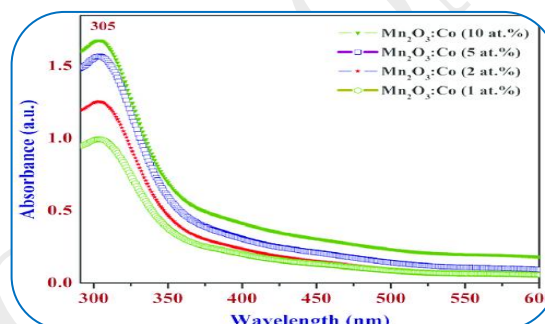
KEYWORDS : *Cobalt, Manganese, Nanoparticles, Composite, Poly (aniline).*

INTRODUCTION

   Manganese Oxide occurs in nature as manganosite and is practically insoluble in water. It dissolves readily in most acids. Synthetic manganese oxide is obtained by reduction of manganese dioxide or by thermal decomposition of manganese carbonate under the exclusion of air. Manganese oxide has major significance as an intermediate in the manufacture of manganese compounds (especially manganese sulfate and sequential products) from MnO_2 ores. MnO_2 is possible cathode for lithium ion batteries (Tompsett et al. 2013). As an important functional metal oxide, manganese dioxide is one of the most attractive inorganic materials because of its physical and chemical properties and wide applications in catalysis, ion exchange, molecular adsorption, biosensor and particularly energy storage (Lu *et al.*, 2015 and Norouzi *et al.*, 2010). Compared with the other transition metal oxide (CuO, Co_3O_4 and NiO, etc.), MnO_2 has been considered as a promising electrode material for LIBs application because of its abundance, low cost and the excellent performance in LIBs as both cathode and anode usage (Li *et al.*, 2006 and Kim *et al.*, 2008). The predominant application of MnO_2 is as component of dry cell batteries, other industrial application includes pigment in glass making (Luo *et al.*, (2016).

   Typical primary batteries include primary Zn–MnO_2, Li–MnO_2, and Mg–MnO_2 batteries. MnO_2 is usually used as cathode materials. The essential obstacle of primary batteries is their low utilization efficiency of the active materials, resulting in low practical capacity and large electrochemical polarization. The development of nanostructured materials offers an interesting strategy to increase the discharge capacity and operating voltage of primary batteries (Zhang *et al.*, 2015 and Lei *et al.*, 2010).

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Particularly, nanostructured current collectors have been designed, fabricated and investigated intensively for supercapacitors (Grote *et al.*, 2014 and Zhao *et al.,* 2015). In addition to high specific surface area to enlarge the electroactive-material or electrolyte interfaces, nanostructured current collectors with rational design can significantly improve the transport characteristics of both charge carriers and ions (Wang *et al.,* 2016). However, the enhancement of MnO conductivity by the external conductive reinforcements is very limited because of the restriction of the MnO_2/conductor interfaces. Doping can improve the performance of oxides (Aliev *et al.,* 2012), mainly focused on metal cations/MnO systems and the resultant improvement in electronic conductivity and capacitance is obscure we propose a novel approach to improving the capacitive performance of thick MnO films by enhancing the intrinsic conductivity of MnO_2 using non-equilibrium doping of free electron metal atoms (such as Au, Ag, Cu, and so on).The free electron metal atoms as electron donors are expected to change the electronic structure of MnO_2 for a better conductivity and high capacitive performance by various characterization of cyclic voltammetry, SEM and powder X-ray diffraction (XRD) (Kang *et al.*, 2013).

The current energy scenario development of new and active materials for next generation energy storage devices is important. Manganese oxides and its derivatives plays vital and important role in electrochemical energy device. The size and morphology also play important role in the storage characteristics. Number of research groups and researchers studied the electrochemical properties of various manganese oxide nanostructures with different structure and shape.

But highly amorphous manganese oxide hydroxide nanomaterials for electrochemical super capacitors are limited. And their composites with intrinsically conducting polymer such as poly(aniline) with manganese oxide hydroxide are rare. Hence, we made an attempt to synthesis the manganese oxide hydroxide by facile room temperature process. The resultant materials were composite with poly(aniline) and the resultant material was tested for the electrochemical supercapacitor application.

MATERIALS AND METHODS
Materials
All chemicals used in this study are Analar Grade from Qualigens and Merck.

Methods
The synthesis of cobalt doped manganese (II) oxide was carried out by ion exchange process and the manganese oxide was prepared by sol-gel method. An aqueous solution of dextrose 0.5 M was quickly added drop wise into 0.05 M potassium permanganate and stirred continuously for 2 hours at room temperature. After getting the brown colored gel, it was washed with double distilled water and dried at 400 °C (Kannan *et al.,* 2011). The resultant blackish brown manganese oxide powder was dispersed in double distilled water and to this solution, an aqueous solution of 0.05 M cobalt (II) nitrate hexahydrate was added with constant magnetic stirring for 24 hours by ion exchange process shows Mn^{2+}Co. After 24 hours, the composite was formed and it was washed several times with double distilled water, filtered and dried at 80 °C (Kim *et al.*, 2014). This dried sample was suspended in poly(aniline), then it was coated on nickel metal plate (2×3mm) carried out in microwave oven for 1 hour at 80 °C.

Characterization
The surface morphology was tested by SEM - FEI Quanta FEG 200-High resolution scanning electron microscope. The crystal structures of the various cobalt and mixed metal oxide thin film on the Nickel plate were characterized by powder XRD (D/max2000, Rigaku miniflex II).

Cyclic Voltammetric Studies:
The electrochemical studies were carried out using CH electrochemical work station with convention three electrode systems. Manganese oxide, Cobalt loaded manganese oxide and Cobalt

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loaded manganese oxide - polyaniline coated on nickel plates are the working electrodes, silver/silver chloride as reference electrode and Platinum electrode as counter electrode (CH608E Austin, USA).

RESULTS AND DISCUSSION
Surface Morphology
The scanning electron microscopic images of the manganese oxide nanoparticles (MnONPs), cobalt loaded manganese oxide nanoparticles (Co-MnONPs) and cobalt loaded manganese oxide nanoparticles incorporated polyaniline (Co-MnONPs-PANI) nanocomposite are shown in Figure 1. The prepared manganese oxide was obtained in nanosize and cobalt loaded manganese oxide nanoparticles was uniformly distributed and the size was found to be approximately 1000 nm. The prepared cobalt loaded manganese oxide nanoparticles were incorporated into polyaniline using nickel plate and produced nanocomposite. The highly dispersed Co-MnONPs over the poly (aniline), the structure of Co-MnONPs slightly changes from amorphous to crystalline nature. Hence, these results clearly gives that cobalt loaded manganese oxide nanoparticles incorporated polyaniline composite was uniform and well dispersed which is mainly helpful for battery storage applications.

X-ray Diffraction
X-ray diffraction for MnONPs, Co-MnONPs and Co-MnONPs–PANI nanocomposite as shown in Figure 1. The main characteristic diffraction peaks at 2θ = 19.2 °, 21.5 °, 25.1 ° and 28.9 ° was assigned (102), (511), (401) and (222) which indicates the formation of hydrated manganese oxide nanoparticles. The cobalt loaded manganese oxide nanoparticles crystallinity was decreased compared to synthesized manganese oxide nanoparticles. The developed Co-MnONPs–PANI nanocomposite crystallinity was decreased compared to MnONPs and Co-MnONPs which confirms the Co-MnONPs was well dispersed in to the nanocomposite. Hence, this result confirms Co-MnONPs–PANI nanocomposite was semi-crystalline in nature which helps for battery storage applications.
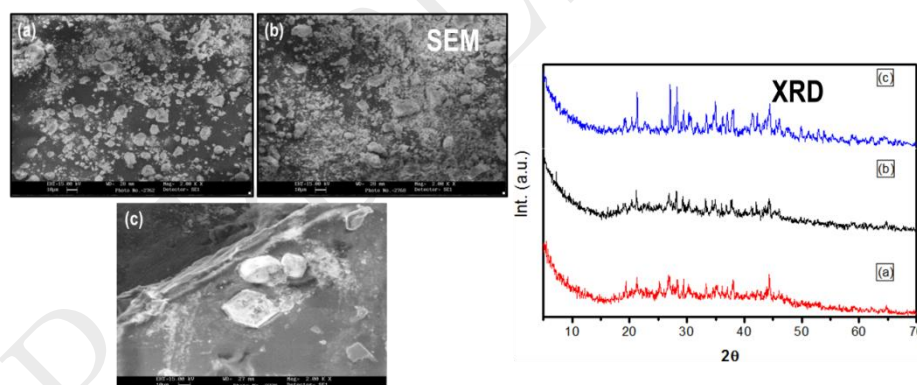

Figure. 1 Scanning electron microscopic image of a) MnONps b) Co-MnO-NPs c) Co-MnO-NPs-PANI nanocomposite and X-ray Diffraction studies for (a) Co-MnO-NPs-PANI nanocomposite b) Co-Mn-NPs and c) MnONPs

Charge- Discharge Studies:
The cyclic voltammetry studies shows slow–charge and fast –discharge behavior which was done using Chronopontentiometry technique (Gao *et al.*, 2010). The charge-discharge measurement was carried out at different scan densities from 0 to 0.5A (vs. Ag/AgCl) using 2M KOH as the electrolyte. Figure 2 shows the charge-discharge curve and which exhibits the symmetric structure of the charge-discharge curves indicates exceptional electrochemical reversibility of Co-MnONPs–PANI thin film on nickel substrate electrodes (Castro *et al.*, 1998).
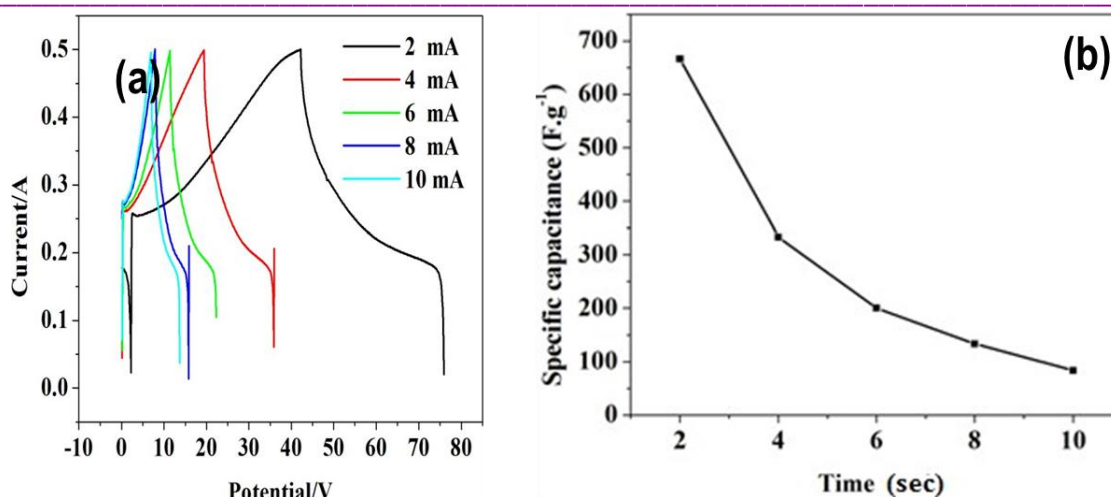
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Figure. 2 (a) Charge-discharge of Co-MnONPs-PANI electrode in 2 M KOH (b) Specific capacitance of Co-MnONPs-PANI electrode from Charge-discharge

The smaller charge-discharge time value is a logical representation of higher OH^- ion redox reversibility resulting from the better surface convenience of OH^- ions (Casella *et al.*, 2002). Charge-discharge curve for the first cycle is not entirely symmetrical, but galvanostatic charge-discharge curves in the following cycles demonstrate highly reversible charge-discharge course and electrochemical capacitive behavior. Figure 2 shows the specific capacitance of Co-MnONPs–PANI at different time intervals during charge-discharge process. It shows the maximum specific capacitance of 680 Fg^{-1} at 2 mVs^{-1}. This is due to the efficient contact between active materials and electrolytes providing more active sites for electrochemical capacitance reaction (Nagamuthu *et al.*, 2013). Further, it is observed that the specific capacitance value 680 Fg^{-1} is larger than that obtained by cyclic voltammetry (i.e. 325 Fg^{-1}). This may be due to the fact that the ions and electrons have enough time to deliver on the film surface during the Faradic redox reaction. The specific energy has been found to be maximum for the film deposited at the current density 2mA owing to its specific capacitance maximum among all the three electrodeposited films . However, the specific power has been determined to be maximum for the film deposited at 2m Vs^{-1} because of less time involved for charging and discharging processes for a constant potential window of chrono charge- discharge curves of the films, which in turn is attributed to microstructure of the film.

SUMMARY AND CONCLUSION

The highly amorphous manganese oxide hydroxide nanomaterial was synthesized by simple room temperature reduction process. The manganese oxide materials formed as nanostructured with uniform size was doped with Co $(NO3)2.6H2O$. The resultant Co doped manganese oxide was composited with PANI and the composite was tested for the electrochemical super capacitor applications. In the formation of Co-MnONPs-PANI composite, the MnONPs changes from crystalline to amorphous nature. The resultant composite shows the maximum capacitance of 680 $F g^{-1}$. The proposed method is facile and the material is active for electrochemical supercapacitor applications. This is first step to develop a flexible supercapacitor at flexible capacitive surface for next generation supercapacitors.

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