7.1 Introduction

Presently researchers are diverted their attention to the preparation of supercapacitor devices using mixed/doped/composite electrodes for high performance devices. Therefore, present chapter aims the use of transition metal oxide electrodes for symmetric supercapacitor device. In the study of manganese and ruthenium doped cobalt oxide thin films ,it was observed that manganese doped cobalt oxide thin film electrodes show high value of SC as compared with pristine cobalt oxide thin film electrode while SC value was decreased for ruthenium doped cobalt oxide thin film electrode.

Therefore, optimized electrode of Mn incorporated Co_3O_4 was used for the preparation of symmetric device for supercapacitor application.

7.2 Experimental

7.2.1 Preparation of Mn incorporated Co_3O_4 symmetric device.

The detail explanation regarding Mn incorporated Co_3O_4 thin films prepared via aqueous medium is given in chapter V. Electrochemical characterization of prepared symmetric device of two electrode system of MnO_2-Co_3O_4 : MnO_2-Co_3O_4 was carried for cyclic voltammetry, chronopotentiometry and impedance spectrometry. The SC, SE, SP and η associated with working electrode were calculated using the relations (3.10), (3.11) and (3.12) as given on chapter III.

7.3 Electrochemical Characterizations

7.3.1 Cyclic voltammetry: Scan rates variation effect

Cyclic voltammograms of symmetric device of MnO_2-Co_3O_4 : MnO_2-Co_3O_4 was carried in 1.0 M KOH electrolyte at different scan rates 2, 5, 10 and 100 mV/s. Fig. 7.1 shows the typical CV curves of symmetric device of MnO_2-Co_3O_4 : MnO_2-Co_3O_4 with redox peak. The results demonstrate the good reversibility and ideal pseudo-capacitive behavior of the electrodes. The CV curves showed the decrease in SC with increase in scan rate (Table 7.1). It is found that SC decrease with scan rates may be because of improper ionic intercalation at higher scan rate which affects the charge storing performance of the

electrode. The maximum SC value obtained is 115.76 F/g at 2 mV/s and 21.23 F/g at 100 mV/s. The results indicate that as the scan rate increases the SC value decreases. This is attributed due to the improper ion intercalation at higher scan rate affects the charge storing performance of the electrodes.

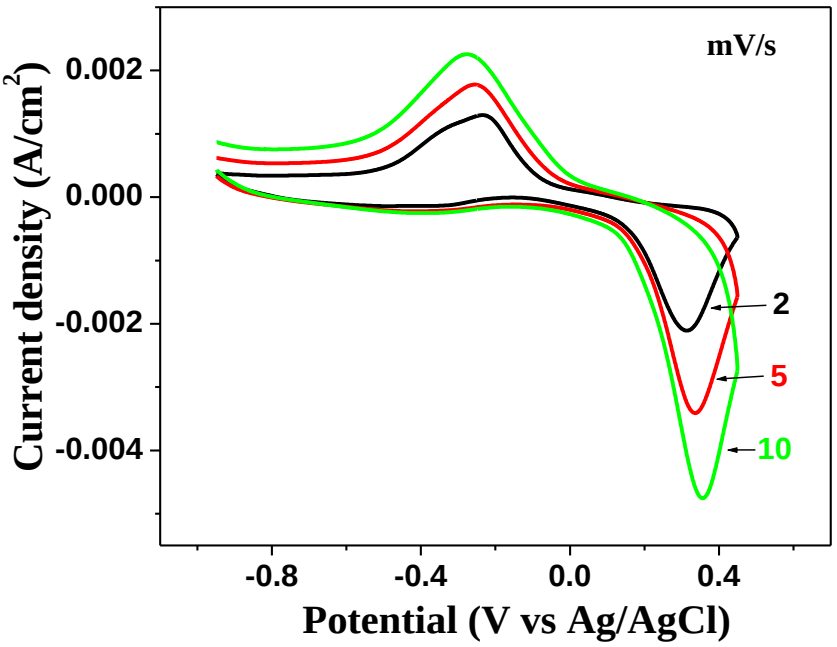

Figure 7.1: CV curves of MnO_2: Co_3O_4 symmetric device carried at different scan rates in 1M KOH.

7.3.2 Stability study

The stability of MnO_2 Co_3O_4 : MnO_2 Co_3O_4 symmetric device was studied in optimized 1.0 M KOH at scan rate 100 mV/s at CV operating potential window – 0.96 to 0.45 V vs Ag/ AgCl. Fig. 7.2 shows the SC vs cycle number variation of MnO_2-Co_3O_4 : MnO_2-Co_3O_4 symmetric device. It is found that intialy SC increases from first cycle (21.23 F/g) to 100 cycle (39.46 F/g) and then shows slow decrement up to 700 cycle (37.05 F/g) and then it remains almost stable with increase in cycle number. Graph shows that there is

no sharp or sudden decrement in the SC value anywhere rather SC increases from first cycle to 100th cycle. It supports strong stability of the device.

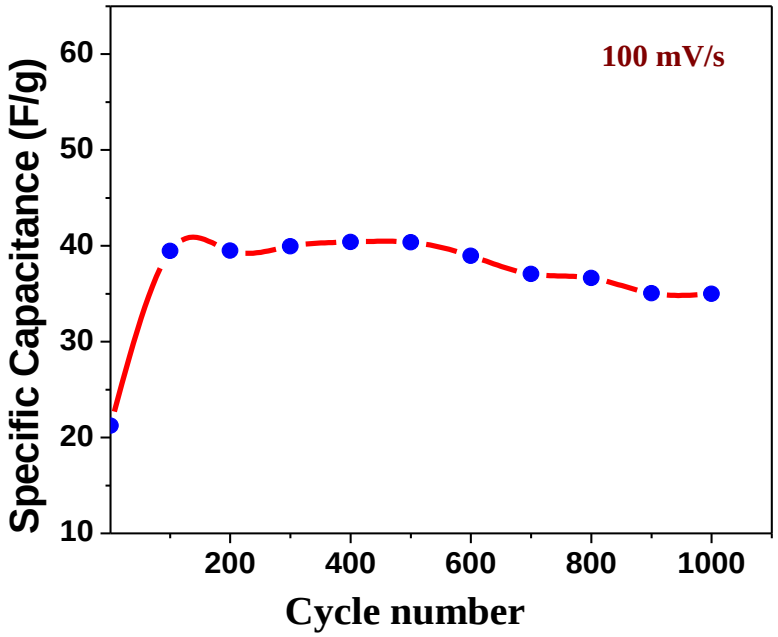

Figure 7.2: Stability curve of $MnCo_3O_4$ symmetric device carried in 1M KOH.

7.3.3 Chronopotentiometry: Charge-discharge curve

Fig.7.3 shows the charge-discharge curves of MnO_2-Co_3O_4 : MnO_2-Co_3O_4 symmetric device at various current densities examined by chronopotentiometry. The asymmetric and non linear nature of charge/discharge curve denotes good pseudocapacitive and irreversible behavior. The electrical parameters, SE, SP and η were calculated using relations reported in chapter III and are tabulated in Table 7.2. It is found that prepared device shows maximum SE 215.81 Wh/kg at 1mA/cm^2, maximum SP 67.44 at 10mA/cm^2 and coulombic efficiency (η%) 90.90 %.

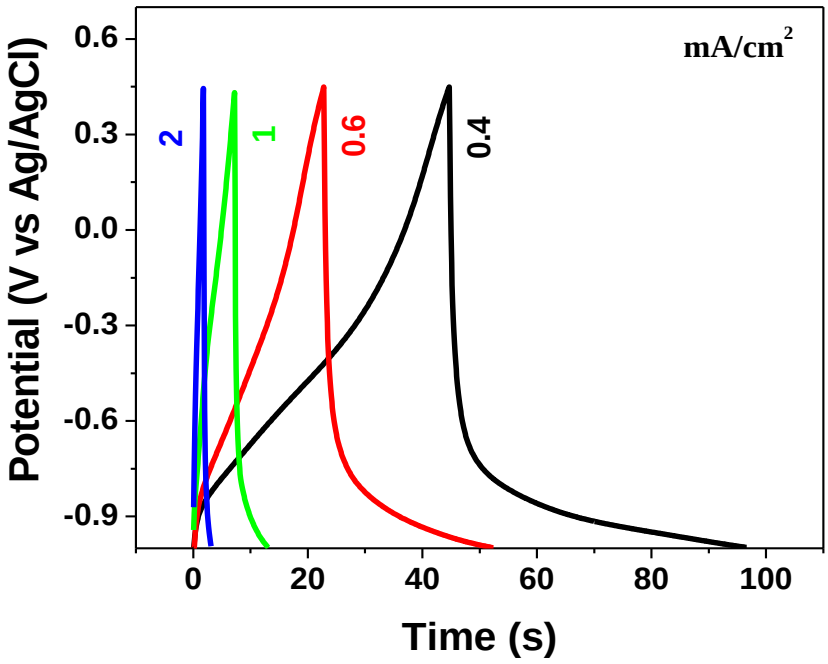

Figure 7.3: Charge - discharge curves of MnO_2 - Co_3O_4 symmetric device observed at different current densities in 1M KOH.

7.3.4 Electrochemical impedance spectroscopy

Using EIS (Electrochemical Impedance Spectroscopy) technique the internal resistance and capacitive behavior of MnO_2-Co_3O_4 : MnO_2-Co_3O_4 symmetric device was observed at the OCP of – 0.658 V in 1 M KOH electrolyte in the frequency range 1 mHz to 1 MHz. Fig.7.4 shows the nyquist impedance plot of (*Z'' vs. Z'*) imaginary *vs.* real impedance. In the high frequency region the crossover point of the highest frequency with the real part of the impedance is a combinational resistance of the electrolyte resistance, intrinsic resistance of the substrate and contact resistance between the active material and the current collector. The internal resistance was around 1.75 Ω. In the intermediate region of frequency, the straight line nature with the inclination of ~45^0 to the real axis was noticed which, in fact the characteristic of ion diffusion in to the electrode materials. Fig.7.5.a) shows matched nyquist plot with experimental and standard curves obtained by

simulation using ZsimpWin software of Co_3O_4 electrode and b) of it shows matched equivalent circuit. The observed circuitry parameters are solution resistance R_1=1.82 Ω, R_2=4.697 Ω, R_3= 6.61 × 10^{11} Ω, C_1 =0.0001717F, C_2 = 0.0002075 F and Q=0.002083F.

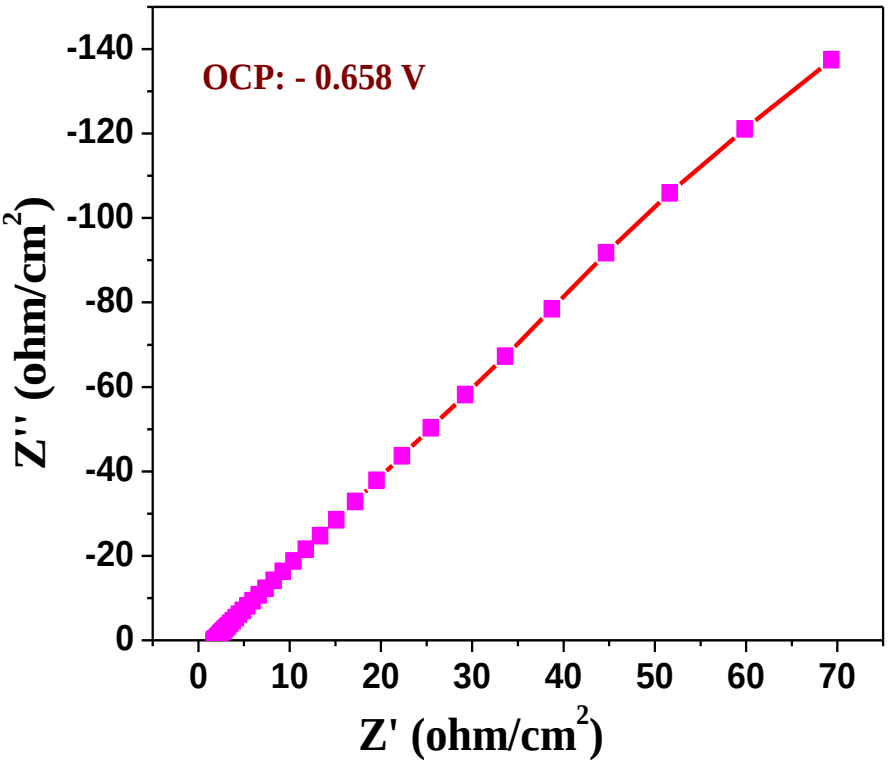

Figure 7.4: Nyquist plot of MnO_2 - Co_3O_4 : MnO_2 - Co_3O_4 symmetric device.

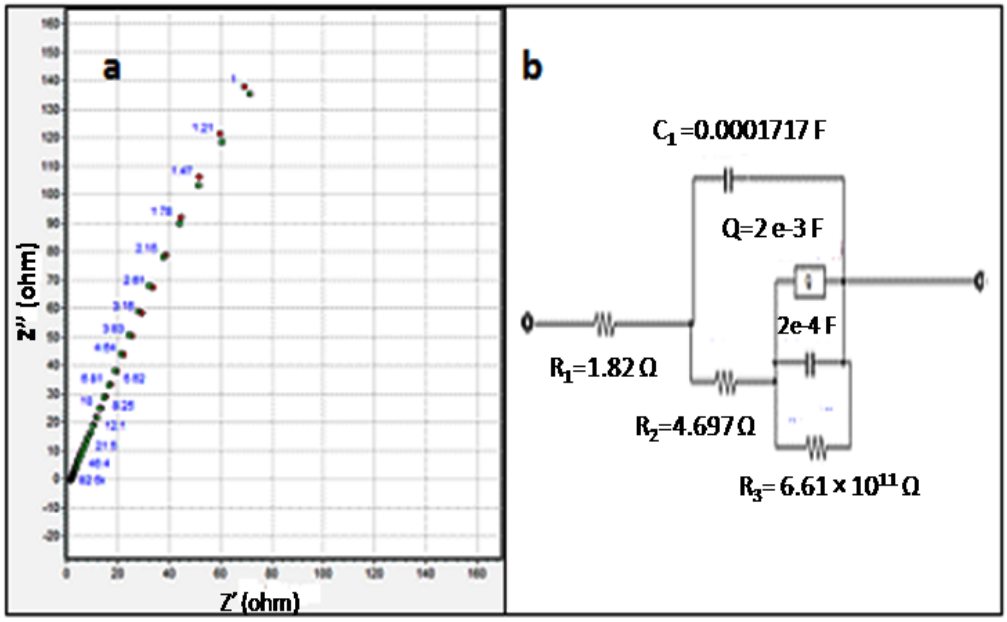

Figure 7.5: a) Matched nyquist plot of MnO_2 - Co_3O_4 : MnO_2 - Co_3O_4 symmetric device.
b) Matched equivalent circuit.

Table 7.1: Variation of SC (F/g) with scan rate for MnO_2 - Co_3O_4 : MnO_2 - Co_3O_4 device.

Scan rate (mV/s)	**2**	**5**	**10**	**100**
SC (F/g)	115.76	71.62	47.90	21.23

Table 7.2: Variation of SE, SP and η at different current densities for MnO_2 - Co_3O_4 : MnO_2 - Co_3O_4 device.

Current density (mA/cm^2)	**Specific energy (Wh/kg)**	**Specific power (W/kg)**	**Efficiency (η %)**
0.4	88.48	2.69	83.01
0.6	59.44	4.04	84.75
0.8	44.24	5.39	76.21
1	215.81	6.74	84.21
2	21.98	13.48	81.98
5	12.08	33.72	71.60
10	7.41	67.44	90.90