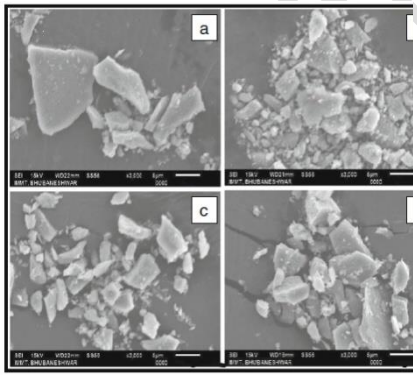
Synthesis of Nano-Electrolytic Manganese Dioxide for Alkaline Batteries Mediated by Organic Additives.

ABSTRACT

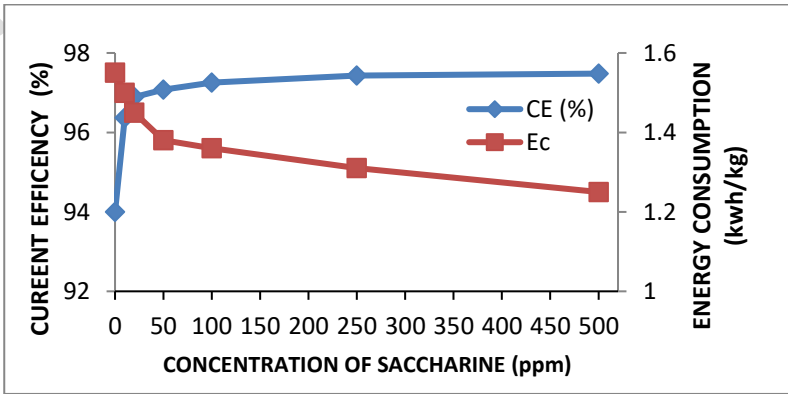
The effect of addition of organic additives such as Glycine(GLY) Sucrose(SUC) and Saccharine(SACCH) on the microstructure and electrical properties of electrolytic manganese dioxide(EMD) produced from an acidic aqueous sulfate solution is discussed. The X-ray diffraction(XRD), scanning electron microscopy(SEM) and Fourier transform infrared spectroscopy(FTIR) were used to determine the structure and chemistry of EMD. The charge-discharge characteristics of the material were determined to evaluate their potential for alkaline battery application. All the EMD samples were found to contain predominantly γ-phase MnO_2, which is electrochemically active for energy storage application. The presence of glycine, sucrose and saccharine as organic additive in the solution increased the current efficiency while decreasing energy consumption during electrochemical deposition of manganese dioxide (MnO_2). The SEM images showed that discrete particles with no agglomeration and small grain size were obtained in the case of EMD deposited with additive while a large grain size was obtained without additives. Charge-discharge characteristics implied the presence of additives enhances the energy storage within the MnO_2 structure. This implied the ability of the additives to affect the particle size and morphology and therefore electrochemical activities of electrodeposited material. The effects in the case of additives investigated in this work were to produce a material with potential application for battery technology.

Key words: Electrolytic manganese dioxide, Additives, Current efficiency, electrochemical activity, Charge-discharge characteristics, Battery application

GRAPHICAL ABSTRACT



SEM pictures of the EMD with and without additives



Organic additives increase current efficiency where as decreases energy consumption.

1. INTRODUCTION

On increasing population growth there is much more demand for energy and improvement in living standard. Normally eighty five percent of total energy is based on limited fossil fuels. So there is a demand for new energy material as well as energy storage devices. Electrolytic

manganese dioxide (EMD) is used as an imperative cathode material which has wide application in rechargeable batteries [1]. The MnO_2 used in batteries is commonly prepared by electro-deposition and hence termed as electrolytic manganese dioxide (EMD). MnO_2 being an environmentally benign and relatively inexpensive as compared to other metal oxide such as nickel and cobalt oxide, has high demand for use in primary and secondary batteries in recent times. The multiple valence states of Mn makes MnO_2 exhibit a very rich electrochemistry and is an attractive material because of the diversity of its crystalline structure[2]. The most suited material for batteries is γ-MnO_2 due to its high intercalation voltage and hence used extensively. However this effectiveness may be elevated by carrying out electrolysis for their production at a suitable interface using various additives. Production of γ-MnO_2 by electrochemical method shows better performance over the chemically produced material.

The physicochemical and electrochemical properties of EMD were mainly influenced by the electrolytic composition H_2SO_4 and the presence of metallic impurities as dopants was explained by discharge-charge capacity[3,4,5,6]. Fletcher et al. [7] reported that nickel and titanium dopant ions are beneficial in terms of attaining excellent rechargeability. Surfactants are commonly used in the preparation of various electrode materials by a number of different techniques, such as chemical co-precipitation and liquid co-precipitation, in addition to electrochemical deposition methods. Alternatively, addition of organic surfactants to the electrolytic cell appears to be an attractive method as well to improve the electrochemical processes at the substrate/electrolytic solution interface. Surfactants play an important role in modifying the growth pattern (and hence structure) of the electrodeposits through adsorption on the electrode surface.The electrochemical behavior of EMD prepared in the presence of surfactants—namely, t-octyl phenoxy polyethoxyethanol (Triton X-100), cetyltrimethylammonium bromide (CTAB), or sodium n-dodecylbenzenesulfonate (SDBS)—is suitable for battery applications and in absence of those MnO_2 prepared does not have properties appropriate for battery applications [8,9]. Among the surfactants Triton X-100 is reported[8] to have most improved the charge/discharge cycle behavior of EMD, possibly due to strong adsorption of the surfactant resulting in an increase in charge acceptance capability and current efficiency (CE) thereby increasing specific capacitance of an energy storage device[10] and suitable for battery applications.The nanoporous/nanocrystalline EMD modified with Brij 56 as surfactant [11]exhibited outstanding cycling stability in addition to better electrochemical performance.

The influence of anionic surfactant such as sodium dodecyl sulphate(SDS) changed the morphologies, reduced the particle size, and increased the specifc surface area as well as the electrochemical and supercapacitive behavior of the MnO_2 samples[12,13].

Avijit et al. [14–16] have reported the effect of series of cationic , non-ionic and anionic surfactants and observed that EMD deposited from a bath containing cationic surfactants such as quaternary ammonium salts were found to be suitable in increasing the current efficiency (CE) and decreasing the energy consumption (EC) of the EMD deposition process. The presence of non-ionic surfactants (Triton X-100 and Tween 20) enhanced the electrochemical activity of EMD, not only by modifying the structure but also by increasing the surface area and porosity of the EMD samples. EMD doped with surfactants have good cycle life in spite of a decrease in initial discharge capacity, relative to surfactant-free EMD. Optimum concentration of surfactant must be essential for the positive consequences in the performance and behaviour of the sample. Anionic surfactant s.a. sodium octyl sulphate, sodium dodecyl sulphate and sodium tetra decyl sulphate strongly influenced crystal morphology by delaying the relative growth rates of MnO_2 particles. Electrochemical studies of the electrodeposited EMD in the presence of STS as a surfactant indicate it is a potential candidate for use as electrode material in alkaline rechargeable batteries.

Due to the rising demand for EMD, continual efforts are underway to find alternative sources from which EMD can be produced with better electrochemical performance.The present work describes a different approach of synthesis of EMD from a synthetic solution in presence of certain organic additives such as glycine, sucrose and saccharine . The work described here the ability of EMD synthesized from synthetic solution (manganese sulphate solution) in presence of organic additives to serve as an electrode material for various charge storage

cells. The aim is to optimize intercalation voltage by choosing accurate additives for their use in the batteries with increase of charge-discharge capacity and current efficiency, decrease of energy consumption, and change of surface morphology. The characteristics such as improved storage capability, cycling stability, safety and economic life-cycle cost could make the device an attractive alternative to conventional charge storage devices using more expensive high-grade materials..

2. MATERIAL AND METHODS:

2.1. SYNTHESIS OF EMD:

Electrolytic manganese dioxide (EMD) was prepared from synthetic aqueous sulfate solutions containing 50 gdm^{-3} $MnSO_4 \cdot 7H_2O$ and 25 gdm^{-3} H_2SO_4 at an anodic current density of 200 Am^{-2} in a glass cell. Organic additives were added at different concentrations (in ppm) into the electrolytic bath during electrolysis. The anodic oxidation of Mn^{2+} to MnO_2 was carried out on a lead (Pb) anode placed in parallel to a stainless steel (SS) cathode. The anode to cathode distance was kept at 2.0 cm. in all experiments. The constant DC source was provided through a regulated power supply system (0-32 V, 10A, Aplab ltd., India).Cell voltage was recorded using a multimeter connected across the anode and cathode. The electrolytic solution was maintained at temperature 90^0C for 6 hrs by using a thermostat and the volume of electrolytic solution was kept constant by adding double distilled water time to time. The electrodeposited MnO_2 was removed from the anode after the deposition period and washed thoroughly with deionized water before drying in an oven. The dried mass was ground and sieved through a 50-µm mesh to obtain EMD powder. Subsequently, the resultant product in powder form was washed repeatedly with deionized water until the sample was sulfate free. The EMD powder was finally dried at 110℃ in an oven for 5 hrs and cooled in desiccators.

2.2. PHYSICAL CHARACTERIZATION:

X-ray diffractograms were recorded for the EMD powders using PAN analytical diffractometer (PW 1830, Philips, Japan) with Cu Kα radiation. The scans were recorded in the 2θ range 5-45 degree. The surface morphology of the EMD samples was determined using field emission scanning electron microscope (FESEM, ZEISS SUPRA 55). Fourier transform infrared (FT-IR) spectrographs were recorded on a Nicolet 6070 spectrophotometer in the frequency range 400–4500 cm^{-1}.

2.3. ELECTROCHEMICAL CHARACTERIZATION:

A suspended cell arrangement was employed for evaluating the electrochemical behavior of the prepared samples. The discharge profile was recorded at room temperature (27± 2 °C) while imposing constant discharge and charge currents in 9 M KOH electrolyte solution. A schematic diagram of the electrolytic cell arrangement for charge–discharge study is given in Fig.1. The experimental cell consisted of a zinc strip (100 × 10 mm) as anode and EMD cathode. The cathode was prepared from a uniform mixture of EMD and graphite powder with polyvinyl alcohol (PVA) as binder. The mixture was placed in a stainless steel mesh to facilitate electrical contact, placed in a die, and then subjected to a pressure of 9,800 kPa by means of a pressure die machine. The resulting EMD was positioned in the cell assembly and allowed to equilibrate for 1hr at its open circuit potential before commencing the electrochemical processes. The applied discharge current was 1 mA with a cut-off voltage (COV) of 0.9 V. The applied charge current was 2 mA with a cut-off voltage of 1.8 V. The discharge capacities were recorded for up to 14 cycles. The galvanostatic measurements were carried out using a BITRODE deep cycle battery tester (LCN1-25-24, USA).

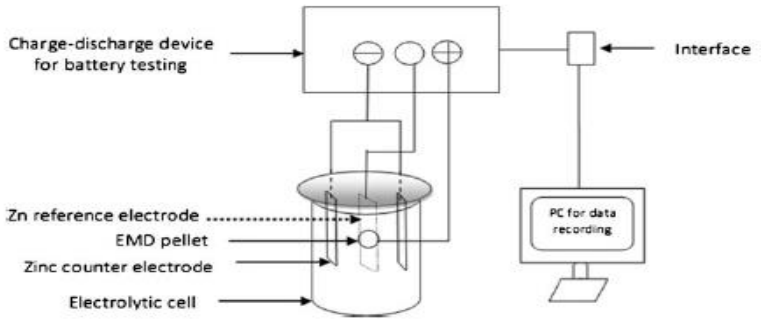


Fig-1: Schematic diagram of electrolytic cell arrangement for galvanostatic measurements (charge–discharge) of electrolytic manganese dioxide (EMD)

3. RESULT

3.1. ELECTROLYSIS:

The electrochemical parameters, current efficiency (CE) and energy consumption (EC), of electrodeposited EMD prepared with and without organic additives are given in Table-1. The additive free bath yields EMD with a CE of 94% and energy consumption of 1.55 kWh kg^{-1}, and with the introduction of additive, the CE increases to a maximum level up to 98% before decreasing on addition of excess of additives. The increase in CE suggests strong adsorption of the additives on the electrode surface [17]. It is worth noting that during EMD deposition at high temperature, hydrogen gas liberated at the cathode carries acidic mist to the air, which is hazardous to health and may cause damage to the environment, particularly at an industrial scale of EMD production. Therefore an attempt has been made to reduce the hydrogen evolution and the energy consumption by using a Pt/C gas diffusion electrode as the cathode during EMD production. The energy consumption also reduces to 1.36, 1.25 and 0.93, kWh kg^{-1} in case of glycine, saccharine and sucrose respectively at 500 ppm of these additives in the electrolyte against the energy consumption of 1.55 kWh kg^{-1} for additive free electrolyte. The variations of current efficiency and energy consumption with the concentration of additives are shown in figure 2, 3 & 4.

In general, the electro deposition of manganese dioxide [18] from an acidic sulfate solution proceeds through the following reactions:

At Anode: $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$ [1]

At Cathode: $2H^+ + 2e^- \rightarrow H_2$ [2]

At the anode, the formation of MnO_2 does not take place in a single step; rather, Mn^{3+} as an intermediate species is first formed [18] together with some solid intermediates such as MnOOH(s) and Mn_2O_3(s). The Mn^{3+} ion, being unstable in hot acidic solution, undergoes a disproportionation reaction forming Mn^{4+} and Mn^{2+}.

$$Mn^{2+}_{sol} \rightarrow Mn^{3+}_{ads} + e^- \quad [3]$$

$$2\,Mn^{3+}_{ads} \rightarrow Mn^{2+}_{sol} + Mn^{4+}_{ads} \quad [4]$$

The Mn^{4+} is converted to solid MnO_2 through a hydrolysis reaction with fast kinetics[19,20], while Mn^{2+} ions remain in solution. During the electrodeposition process Mn^{3+} ions may be trapped in the MnO_2 lattice, possibly resulting in defects in the crystal structure. Adsorption of surfactants at the substrate/electrolytic solution interface may inhibit the rate of Eq. (3) due transfer kinetics mostly depend on the degree of coverage of the electrode due to either mechanical blocking or through electrostatic interactions[17] to the blocking of the active growth sites, thereby allowing electrodeposition preferentially on the crevices [21]. The electron/ ion This could change the electrical double layer characteristics and thus affect the interfacial energy, dielectric constant, potential, and current distribution at the electrodes resulting in modified crystal growth. Hence, the organic surfactants play a vital role in facilitating the formation of compact deposits with greater surface area. However, careful monitoring of appropriate surfactant concentration during electrolysis is required to

achieve reproducibility. Higher concentrations may lead to irregular morphology owing to higher ohmic potential drop and electrode overvoltage[22]**.**

Table-1: Effect of additives on the electrodeposition characteristics of electrolytic manganese dioxide (EMD)

Additive ($mgdm^{-3}$)	Glycine		Saccharine		Sucrose	
	CE (%)	EC($kWh\ kg^{-1}$)	CE (%)	EC($kWh\ kg^{-1}$)	CE (%)	EC($kWh\ kg^{-1}$)
0	94.00	1.55	94.00	1.55	94.00	1.55
10	96.22	1.51	96.37	1.50	96.54	1.27
20	96.68	1.46	96.89	1.45	96.98	1.24
50	97.98	1.43	97.08	1.38	97.73	1.23
100	98.23	1.37	97.25	1.36	98.06	1.21
250	98.37	1.36	97.43	1.31	98.29	1.16
500	98.51	1.47	97.48	1.25	98.42	0.93
1000	98.57	1.50				
5000	78.73	1.64				

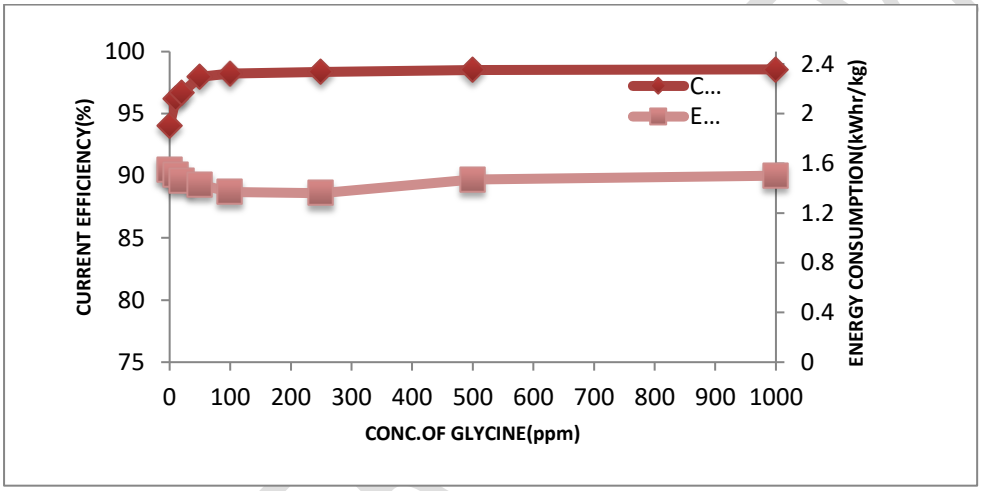


Fig.2: Variation of CE and EC with glycine concentration

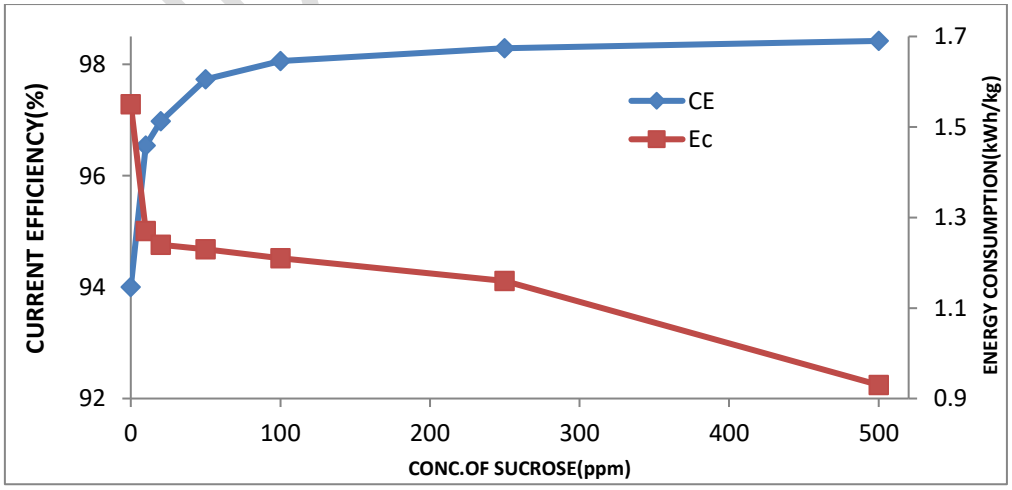


Fig.3: Variation of CE and EC with Sucrose concentration

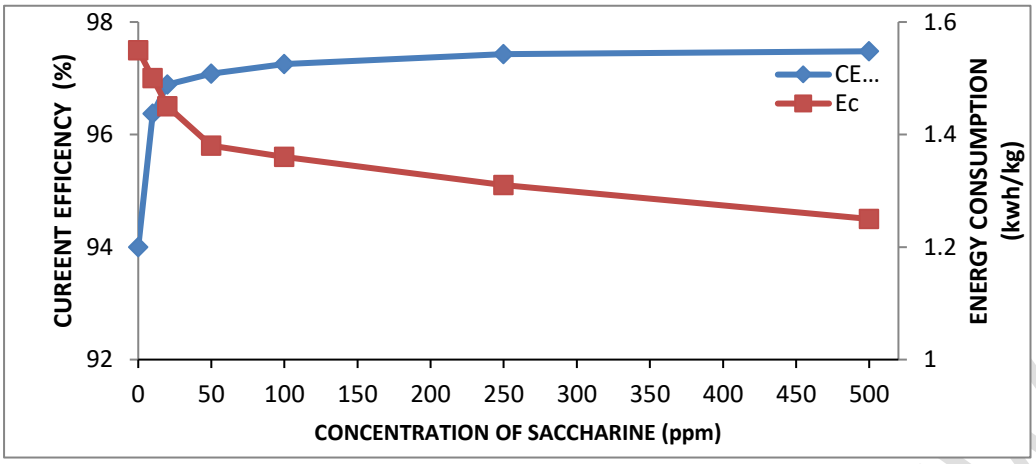


Fig.4: Variation of CE and EC with Saccharine concentration

3.2. X-RAY DIFFRACTION ANALYSIS:

The most common forms of MnO_2 (γ, ε, and β-MnO_2) are related to the mineral structures ramsdellite, akhtenskite, and pyrolusite with orthorhombic, hexagonal, and tetragonal modifications of MnO_2, respectively. The γ and ε forms are electrochemically active [23]. In the present study, all the electrodeposited MnO_2 samples were subjected to X-ray diffraction analyses (Fig. 5) were consistent with hexagonal γ-MnO_2 having lattice parameters a=6.36 Å, b=10.15 Å, and c=4.09 Å (ICDD-JCPDS No. 14-0644) [24,31]. The XRD pattern for the sample prepared in the absence of additive yielded diffractive peaks assigned to the (120), (131), (300), (160), and (421) planes. Addition of as much as 100 ppm organic additive (GLY, SUC and SACCH) did not affect the crystal structure and pattern of the produced EMD materials(Fig.5 b–d). Similarly, lower quantities of additives (~50 ppm) did not produce changes in crystal structure or reflections suggesting that the quantity of additives does not modify the structure. Note that the broad diffraction peaks in the patterns indicate that crystallite size within the EMD samples is within a range suitable for exploitation of the material for high power applications [24]. A very narrow diffraction peak indicates larger particle sizes, which may not be suitable for rechargeable battery applications due to lower surface area.

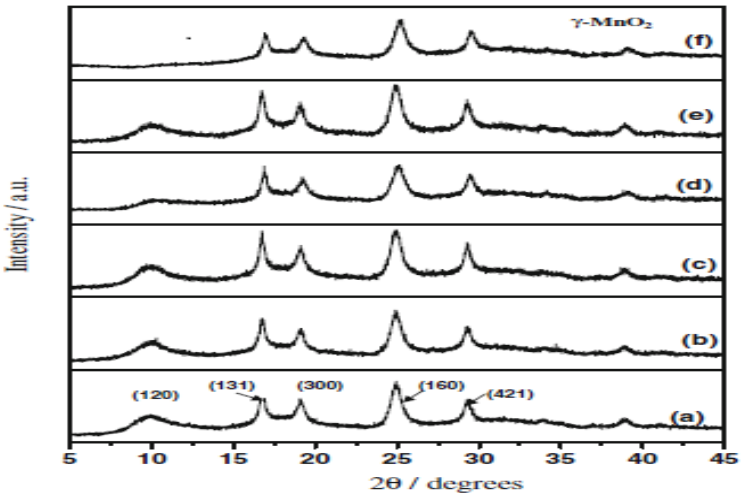


Fig. 5 XRD patterns of EMD (a) No additives (b) 100 ppm Glycine, (c). 100 ppm Sucrose, (d) 100 ppm Saccharine (e) 50 ppm Glycine (f) 50 ppm Sucrose

3.3. FT-IR ANALYSIS:

The FTIR spectrum recorded for the EMD samples (Fig. 6) with and without organic additives at different frequency range. The peak detected in the finger print region of 400–600 cm^{-1} confirms the formation of γ-MnO_2. The broad peak located at about 760 cm^{-1} was assigned to the characteristic peak of MnO_6 octahedron, while the transmission band at 1100 cm^{-1} was attributed

to the MnO_2 stretching mode and/or O-H bending vibrations [25] associated with hydrogen bonding, indicating the presence of bound water molecules [26,27].The strong band at ~1630 cm^{-1} was due to O-H bending vibrations associated with the water of crystallization and a broad band at ~3400 cm^{-1} is due to OH stretching vibration. A weak band is observed at~1400 cm^{-1} indicating O-H stretching vibrations[28]. FTIR data indicate that Glycine , Sucrose and Saccharine addition at the concentrations used in this study had no significant effect on EMD structure and composition. The absence of the characteristic peaks of the organic functional groups of the organic additive suggests that there was no residual additives present after the washing procedure [27].

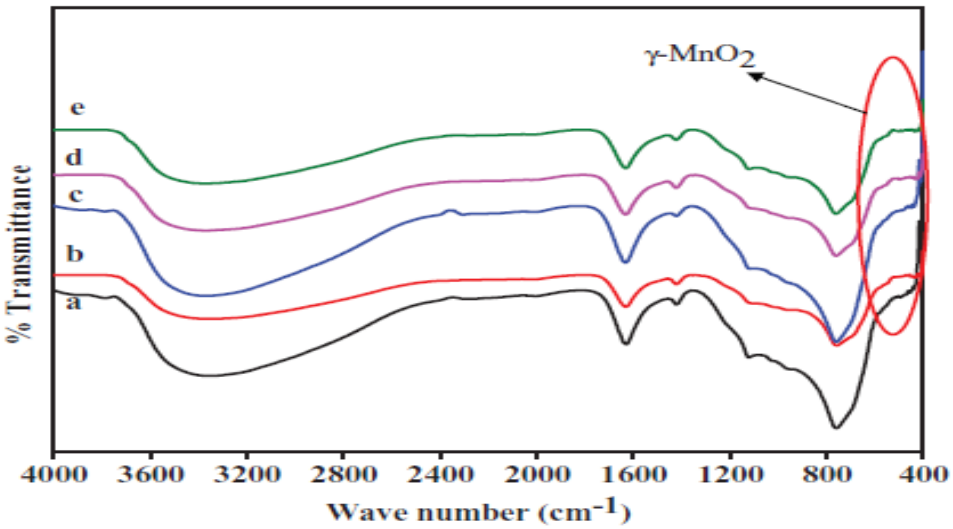


Fig.6: FTIR spectra of EMD (a) No additives, (b) Gly 100 ppm, (c) Sucrose 100 ppm, (d) Saccharine 100 ppm, and (e) Glycine 50 ppm.

3.4. SEM ANALYSIS:

Changes in deposit morphology may influence the current efficiency, stability, and rechargeability of EMD[8]. Surfactants have a significant effect on the deposit pattern due to their control on nucleation and growth mechanisms during electrodeposition [29], as well as various interactions with the species present in the electrolytic solutions[30]. The presence of the organic additives in the electrolysis bath influenced the EMD particle size (Fig. 10). Discrete particles with no agglomeration and small grain size are observed in the case of 100 ppm Glycine and Sucrose added (Fig.7 b–c), while a larger grain size is observed for EMD deposited in the absence of additives (Fig.7 a). This suggests that the organic additives have promoted nucleation and current distribution during electrodeposition, resulting in the observed increase in current efficiencies (CE) of the EMD samples (Table 1) and the associated decrease in power consumption during electrodeposition in all cases. However, for EMD electrodeposited in the presence of Saccharine, a larger particle size distribution was observed.

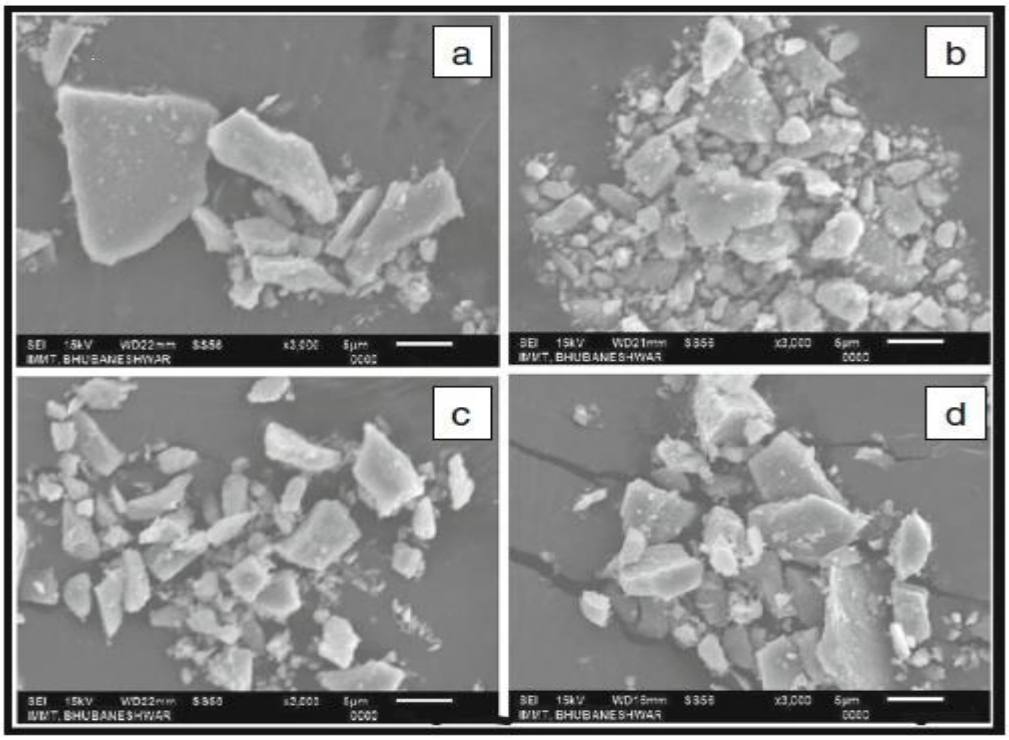


Fig. 7: SEM images of EMD samples prepared from a bath (a) No additives (b) Gly 100 ppm(c) Suc 100 ppm and (d) Sacch 100 ppm

3.5. ELECTROCHEMICAL ACTIVITY:

The electrochemical behavior of the EMD samples was characterized by galvanostatic experiments. The charge and discharge characteristics enable evaluation of the suitability of the prepared EMD as a battery material. The EMD samples prepared in the absence and presence of organic additives were subject to charge–discharge reactions in 9 M potassium hydroxide aqueous solutions. The reactions at cathode and anode are as follows:

Cathode : $MnO_2 + H_2O + e^- \rightleftharpoons MnOOH + OH^-$ [1]

Anode : $Zn + 2OH^- \rightleftharpoons ZnO + H_2O + 2e^-$ [2]

Net Reaction : $Zn + 2MnO_2 + H_2O \rightleftharpoons ZnO + 2MnOOH$ [3]

The electron discharge from MnO_2 is thought to proceed by a homogeneous reversible reaction by the movement of protons and electrons into the lattice, resulting in a gradually decreasing value of x in MnO_x, from x =2.0 to 1.5 [27]. This could be possible due to the conversion of MnO_2 into MnOOH in the solid phase. The second electron discharge of MnO_2, which proceeds either in solid or in solution phase, leads to the formation of $Mn(OH)_2$, a product formed during recharging of γ- MnO_2 [19]. The formation of the discharged products is reported to be nonreversible. This system is, therefore, suitable only as a use and dispose battery. The typical discharge characteristics of the pellets made from EMD powders prepared from aqueous sulfate solutions in the absence and presence of organic additives Glycine, Sucrose , and Saccharine are shown in figures 8- 11.

The discharge capacity of 240 mAh g^{-1} (870 C g^{-1}) was obtained from the EMD containing no additives, against 160 mAh g^{-1} (580 C g^{-1}) for the reported values for EMD in the absence of additives [31]. It is very interesting to note that the addition of organic additives to the electrolytic cell during electrodeposition of MnO_2 produced a significant effect on the discharge performance of the EMD. Addition of glycine increased the discharge capacity to 298 mAh g^{-1} .The EMD prepared in the presence of the other additives (sucrose and saccharine), in the electrolytic solutions at concentrations of 100 ppm, showed discharge capacities of 278 and 275 mAh g^{-1}, respectively. It is also interesting to note that the discharge capacity of the EMD prepared in the absence of additive fades rapidly (Fig. 8a). However, EMD prepared in the presence of organic additives was able to maintain discharge capacity over a greater number of cycles (Fig. 8b–d).

Addition of 10 ppm and 50 ppm glycine (Fig. 9b–c) increased the initial discharge capacity to 285 and 290 mAh g^{-1}, respectively, from approximately 245 mAh g^{-1} for the EMD prepared with no additives present. A further increase in the concentration of glycine to 100 ppm (Fig. 9e) increased the discharge capacity to a maximum of 298 mAh g^{-1}. However, further increasing the concentration of glycine to 250 ppm (Fig. 9d) caused a lowering of the discharge capacity to 234 mAh g^{-1}.

A similar behavior was observed for both 10 ppm of sucrose and saccharine (Fig. 10b and 11b), where initial discharge capacities of 259 and 251 mAh g^{-1} were obtained respectively. The EMD prepared in the presence of these additives in the electrolytic solution at concentrations of 100 ppm showed initial discharge capacities of 278 and 275 mAh g^{-1} respectively, while again a concentration of 100 ppm for these additives decreased the discharge capacities, in these cases to 252 and 233 mAh g^{-1} for sucrose and saccharine, respectively. The data obtained in this study suggest that the use of glycine and sucrose during the electrodeposition of manganese dioxide is beneficial in terms of cycle stability and discharge capacity.

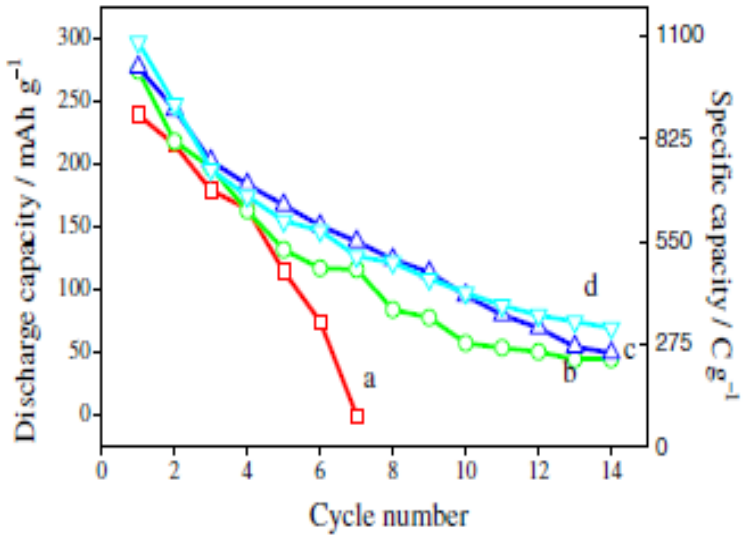


Fig.8: Discharge and specific capacity versus cycling behavior of EMD samples with (a) No additive (b) 100 ppm Saccharine.(c) 100 ppm Sucrose (d) 100ppm Glycine.

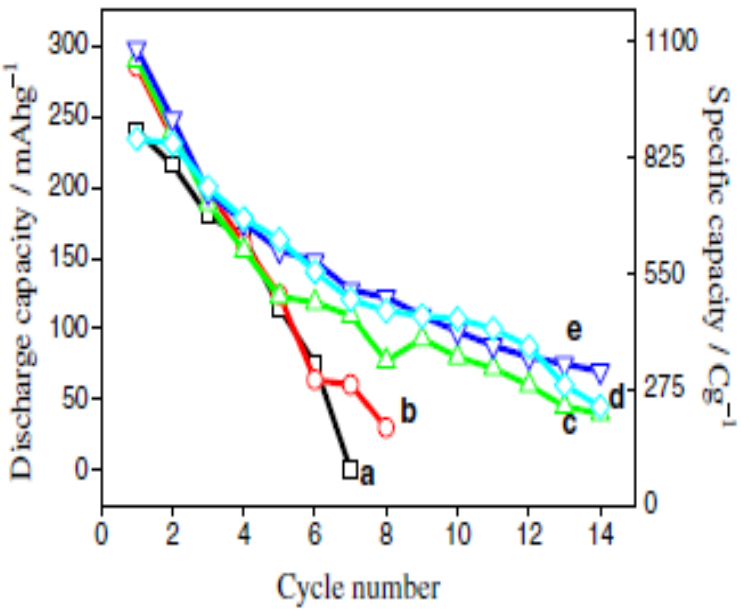


Fig.9: Discharge and specific capacity versus cycling behavior of EMD samples containing Glycine in different concentration. (a) 0 (b) 10 (c) 50 (d) 250 and (e) 100 ppm.

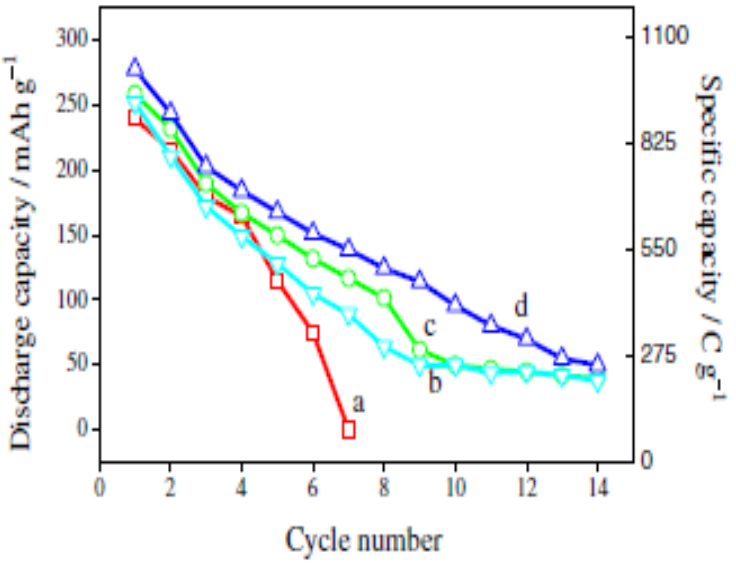


Fig.10: Discharge and specific capacities versus cycling behavior of EMD samples containing sucrose in different concentration (a) 0 (b) 10 (c)100 and (d) 50 ppm

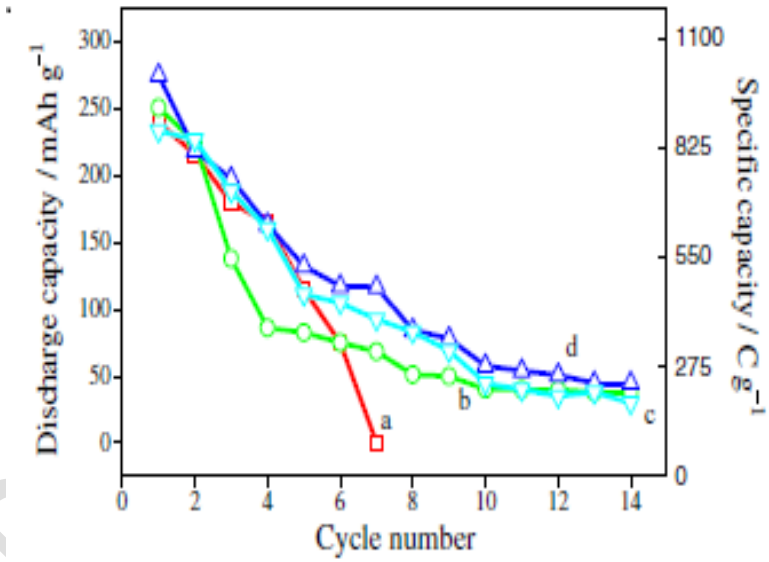


Fig.11: Discharge and specific capacities versus cycling behaviour of EMD samples containing sucrose in different concentration (a) 0 (b) 10 (c) 100 and (d) 50 ppm

4. CONCLUSION

The organic additives played a vital role in modifying crystal morphology and hence current efficiency and energy consumption depends on the type and actual concentration of the additive used. The presence of glycine sucrose and saccharine as organic additives during the electrodeposition of MnO_2 has not affected the crystal pattern of the synthesized EMD samples and all the samples show the characteristics of γ-MnO_2. There is an increase in current efficiencies of the EMD material and decreased the energy consumption of the electrodeposition cell resulting from organic additives. The organic additives influenced the discharge performance of the EMD significantly by increasing the discharge capacities of the material from ~ 240 mAh g^{-1} (870 Cg^{-1}) for EMD prepared without additives to ~290 mAh g^{-1} (1,050 Cg^{-1}) for EMD prepared in the presence of glycine and sucrose, and ~275 mAh g^{-1} (995 Cg^{-1}) in the presence of saccharine.The electrochemical properties of EMD were enhanced by the presence of these additives during electrodeposition and the material produced by these methods had potential for battery applications.

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