

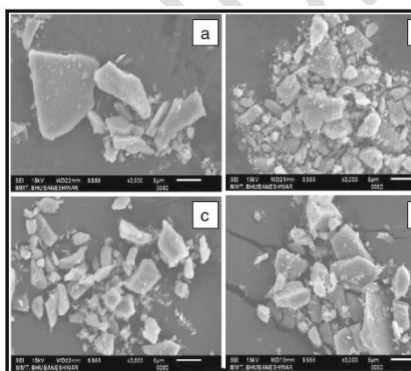
Synthesis of Nano-Electrolytic Manganese Dioxide for Alkaline Batteries Mediated by Organic Additives

ABSTRACT

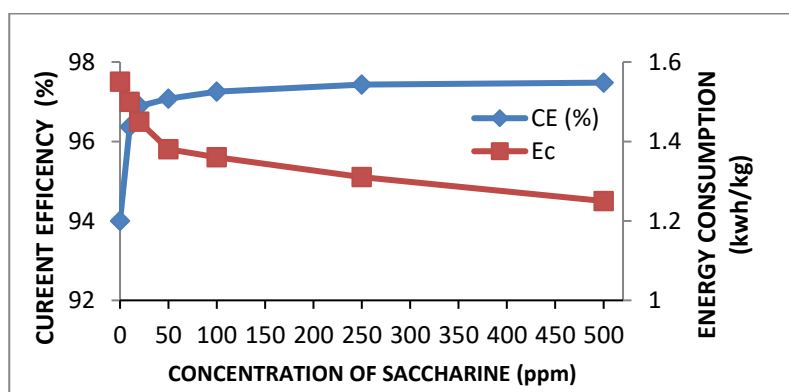
This article discusses the impact of adding organic additives like glycine (GLY), sucrose (SUC), and saccharine (SACCH) on the electrical characteristics and microstructure of electrolytic manganese dioxide (EMD), which is made from an acidic aqueous sulphate solution. The structure and chemistry of EMD were ascertained by means of Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). To assess the material's potential for use in alkaline batteries, its charge-discharge properties were ascertained. It was found that the majority of MnO_2 in all the EMD samples was in the γ -phase, which is electrochemically active and useful for energy storage applications. When glycine, sucrose, and saccharine were added to the solution as organic additives, the electrochemical deposition of manganese dioxide (MnO_2) resulted in an increase in current efficiency and a decrease in energy consumption. The SEM images demonstrated that when EMD was deposited with an additive, small grain sizes and discrete particles free of agglomeration were formed, but large grain sizes were obtained in the absence of additives. Charge-discharge characteristics suggested that the additions improve the ability of MnO_2 structure to store energy. This suggested that the additions may have an impact on the morphology and size of the particles, and consequently, the electrochemical activities of the material that was electrodeposited. In the case of the additives examined in this paper, the outcome was the creation of a material with possible use in 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

There is a greater need for energy as the population grows and living standards rise. Normally, the use of finite fossil fuels accounts for 85% of the world's energy. Thus, there is a need for both energy storage technologies and novel energy sources. In rechargeable batteries, electrolytic manganese dioxide (EMD) is a necessary cathode material with a broad range of applications [1]. Electrolytic manganese dioxide (EMD) is the designation for the MnO_2 that is widely generated by electro-deposition and utilized in batteries. MnO_2 is in high demand for usage in primary and secondary batteries these days since it is an environmentally friendly and reasonably priced metal oxide when compared to other oxides like nickel and cobalt oxide. Because of the variety of its crystalline structure and the variable valence states of Mn, MnO_2 exhibits a very rich electrochemistry and is a material that is interesting [2]. Because of its high intercalation voltage, $\gamma\text{-MnO}_2$ is the most suitable material for batteries and is therefore widely employed. However, by conducting electrolysis for their formation at an appropriate interface with different additives, its effectiveness may be increased. The electrochemical approach of producing $\gamma\text{-MnO}_2$ exhibits superior performance compared to the material produced chemically.

Physicochemical and electrochemical properties of EMD were mostly controlled by the sulfuric acid electrolyte, and the presence of metallic impurities (dopants) as explained by discharge-charge capacity [3,4,5,6]. Fletcher et al. [7] found that nickel and titanium dopant ions improve rechargeability. Surfactants are commonly utilised to manufacture diverse electrode materials using a variety of procedures, including chemical and liquid co-precipitation, as well as electrochemical deposition methods. Alternatively, adding organic surfactants to the electrolytic cell looks to be a promising technique for improving electrochemical processes at the substrate/electrolytic solution interface. Surfactants influence the development pattern (structure) of electrodeposits by adsorption on the surface of the electrode. The electrochemical behaviour of EMD is suitable for battery applications prepared in the presence of surfactants like t-octyl phenoxy polyethoxy ethanol (Triton X-100), cetyl trimethyl ammonium bromide (CTAB), or sodium n-dodecyl benzene sulfonate (SDBS), whereas in absence of those does not have battery-suitable properties [8,9]. Among the surfactants, Triton X-100 is reported [8] to have most improved the charge/discharge cycle behaviour of EMD, possibly due to better adsorption of the surfactants, resulting in an increase in charge acceptance capability and current efficiency (CE), thereby increasing the specific capacitance of an energy storage device [10] and suitable for battery applications. The nanoporous/nanocrystalline EMD treated with Brij 56 as a surfactant [11] shown superior cycling stability as well as improved electrochemical performance.

The anionic surfactant, such as sodium dodecyl sulphate (SDS), altered the morphologies, reduced particle size, increased specific surface area, and altered the electrochemical and supercapacitive behaviour of MnO_2 samples [12,13]. Avijit et al. [14-16] worked on the effect of cationic, non-ionic, and anionic surfactants and observed that cationic surfactants (quaternary ammonium salts) most effectively increased current efficiency (CE) and decreased energy consumption (EC) of the EMD deposition process. The non-ionic surfactants (Triton X-100 and Tween 20) improved electrochemical activity by changing the structure as well as increasing the surface area and porosity of the samples. EMD doped with surfactants has a longer cycle life than surfactant-free EMD, despite having a lower initial discharge capacity. The optimal surfactant concentration must be required for the sample to perform and behave positively. Anionic surfactants such as sodium octyl sulphate, sodium dodecyl sulphate, and sodium tetradecyl sulphate had a considerable influence on crystal shape by delaying the relative growth rates of MnO_2 particles. Electrochemical tests of electrodeposited EMD in the presence of SDS as a surfactant show that it is a promising candidate for use as an electrode material in alkaline rechargeable batteries [32].

The present work designed to find alternative sources from which EMD can be produced with better electrochemical performance because of the rising demand for EMD. A different approach described the 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 $50 \text{ gdm}^{-3} \text{ MnSO}_4 \cdot 7\text{H}_2\text{O}$ and $25 \text{ gdm}^{-3} \text{ H}_2\text{SO}_4$ at an anodic current density of 200 Am^{-2} in a glass cell. Organic additives viz. Glycine, Saccharine and Sucrose were added at different concentrations (10-500 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°C 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 separated from the anode after the deposition and washed thoroughly with deionized water and dried. Then the dried mass was ground and sieved through a $50\text{-}\mu\text{m}$ mesh to obtain EMD powder. Ultimately, 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°C for 5 hours and cooled in desiccators.

2.2. PHYSICAL CHARACTERIZATION:

The prepared EMD powders was subjected to X-ray diffractograms (PAN analytical diffractometer PW 1830, Philips, Japan) with $\text{Cu K}\alpha$ radiation. The scans were recorded in the 2θ range $5\text{-}45$ degree. Field emission scanning electron microscopy (FESEM, ZEISS SUPRA 55) determined surface morphology. Fourier transform infrared (FT-IR) spectrographs were recorded on a Nicolet 6070 spectrophotometer in the frequency range $400\text{-}4500 \text{ cm}^{-1}$.

2.3. ELECTROCHEMICAL CHARACTERIZATION:

The electrochemical behaviour such as discharge profile of the generated samples was measured at room temperature ($25 \pm 2^\circ\text{C}$) with constant discharge and charge currents in a 9 M KOH electrolyte solution. The Figure 1 depicts a schematic design of the electrolytic cell setup used for charge-discharge studies. The experimental cell used a zinc strip ($100 \times 10 \text{ mm}$) as an anode and an EMD cathode, made from a homogeneous mixture of EMD and graphite powder, with polyvinyl alcohol (PVA) as a binder. The mixture was placed in a stainless steel mesh to allow electrical contact and subjected to a pressure of 9,800 kPa using a pressure die machine. The generated EMD was placed in the cell assembly and left to equilibrate at its open circuit potential for 1 hour before beginning the electrochemical procedures. The discharge current used was 1 mA, with a cut-off voltage of 0.9 V. The applied charge current was 2 mA, with a cut-off voltage of 1.8 V. The discharge capacity was measured for up to 14 cycles.

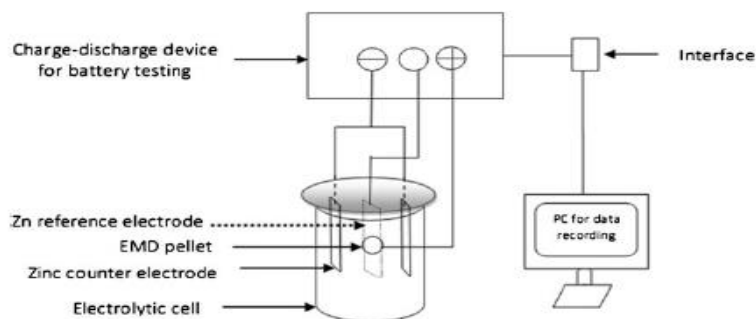


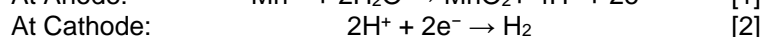
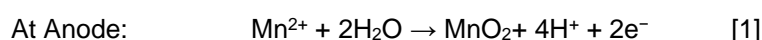
Fig-1: Galvanostatic measurements using Electrolytic cell arrangement .

3. RESULT

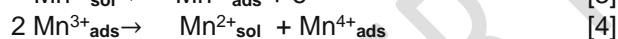
3.1. ELECTROLYSIS:

The electrochemical parameters, current efficiency (CE) and energy consumption (EC), of electrodeposited EMD prepared with and without organic additives are given in Table-1. With no additive a CE of 94% and energy consumption of 1.55 kWh kg⁻¹ was attained by EMD, whereas with additive, the CE increased up to a maximum level 98% which decreased on addition of excess additives. The increase in CE suggested a strong adsorption of additives on the electrode surface [17]. A Pt/C gas diffusion electrode was used as the cathode to reduce the hydrogen evolution and the energy consumption during EMD production because hydrogen gas liberated at the cathode is hazardous and may cause environmental damages. The energy consumption also reduced to 1.47, 1.25 and 0.93, kWh kg⁻¹ in case of glycine, saccharine and sucrose respectively when 500 ppm of these additives were used in the electrolyte. The energy consumption is 1.55 kWh kg⁻¹ when no additives were used. The variations of current efficiency and energy consumption with the concentration of additives are shown in Fig. 2, 3&4.

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



At the anode, the formation of MnO₂ does not take place in a single step; rather, Mn³⁺ as an intermediate species is first formed [18] together with some solid intermediates such as MnOOH(s) and Mn₂O₃(s). The Mn³⁺ ion, being unstable in hot acidic solution, undergoes a disproportionation reaction forming Mn⁴⁺ and Mn²⁺.



The Mn⁴⁺ is changed to solid MnO₂ through a hydrolysis reaction with fast kinetics [19,20], while Mn²⁺ ions remained in solution. During the electrodeposition process Mn³⁺ ions may be trapped in the MnO₂ lattice, possibly resulting in defects in the crystal structure. Surfactant adsorption at the substrate/electrolytic solution contact may resist the rate of transfer resulted from Eq. (3). Kinetics are primarily determined by the rate of electrodeposition caused by mechanical or electrostatic interactions [17], which block active growth sites, allowing electrodeposition preferentially on crevices [21]. The electrical double layer characteristics were altered by this process influencing the interfacial energy, dielectric constant, potential, and current distribution at the electrodes, resulting in altered crystal formation. Thus, organic surfactants play an important function in encouraging the formation of compact deposits with a larger surface area [32]. To achieve reproducibility, it is necessary to carefully monitor the optimum surfactant concentration during electrolysis. Higher concentrations may lead to irregular morphology owing to higher 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

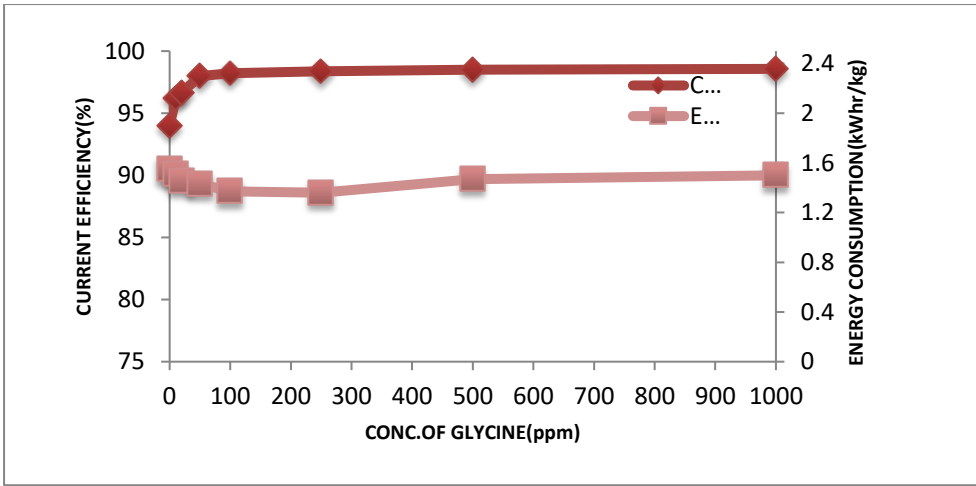


Fig.2: Variation of CE and EC with glycine concentration

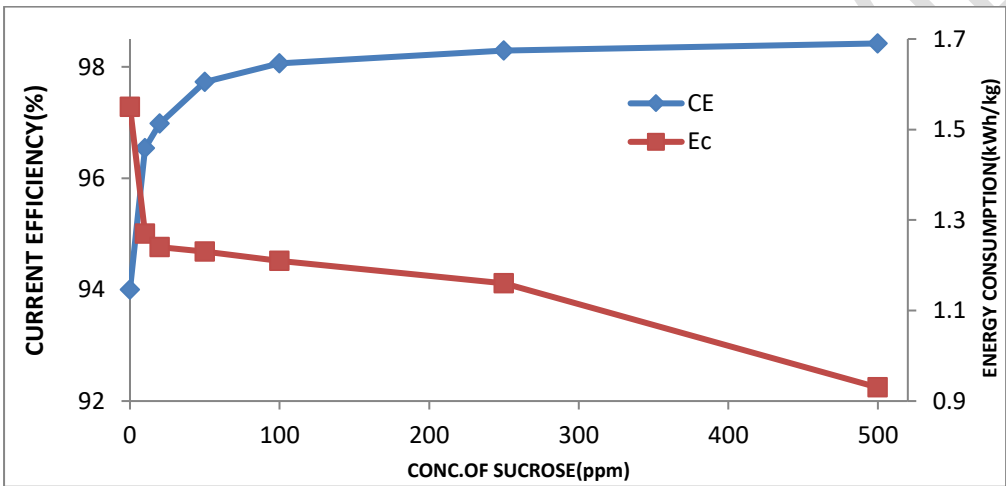


Fig.3: Variation of CE and EC with Sucrose concentration

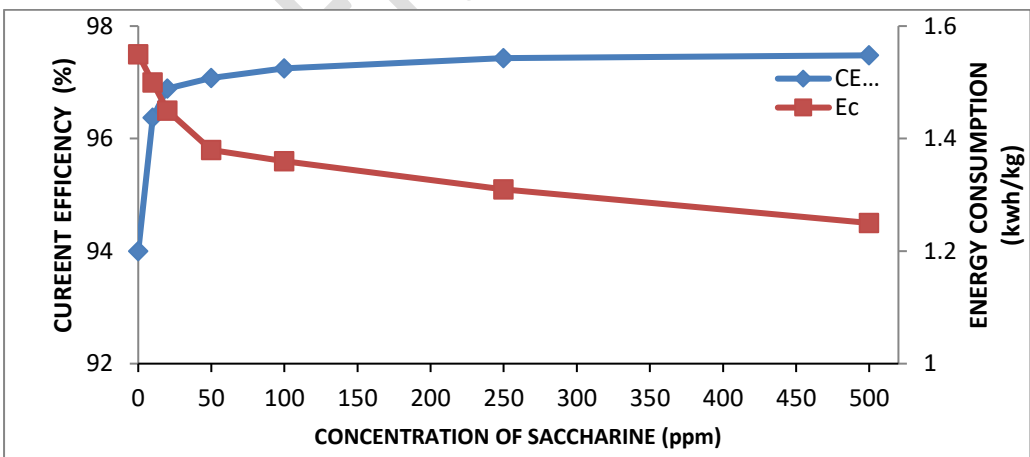


Fig.4: Variation of CE and EC with Saccharine concentration

3.2. X-RAY DIFFRACTION ANALYSIS:

The three most prevalent forms of MnO_2 (γ , ϵ , and β - MnO_2) are associated to the mineral formations ramsdellite, akhtenskite, and pyrolusite with orthorhombic, hexagonal, and tetragonal

modifications of MnO_2 , respectively. The γ and ϵ forms exhibit electrochemical activity [23]. X-ray diffraction analysis of electrodeposited MnO_2 samples (Fig. 5) revealed hexagonal $\gamma\text{-MnO}_2$ with lattice parameters $a=6.38 \text{ \AA}$, $b=10.05 \text{ \AA}$, and $c=4.12 \text{ \AA}$ (ICDD-JCPDS No. 14-0644) [24, 31]. diffractive peaks in case of no additives are attributed to the (120), (131), (300), (160), and (421) planes. The addition of up to 100 ppm organic additives (GLY, SUC, and SACCH) had no effect on the crystal structure or pattern of the generated EMD materials (Fig. 5 b-d). Lower amounts of additives ($\sim 50 \text{ ppm}$) did not alter crystal structure, indicating that the amount of additives did not affect the structure. The large diffraction peaks in the patterns imply that the crystallite size within the EMD samples is within a range that allows the material to be used for applications [24]. A extremely narrow diffraction peak suggests bigger particle sizes, which may be unsuitable for rechargeable battery applications due to their low surface area.

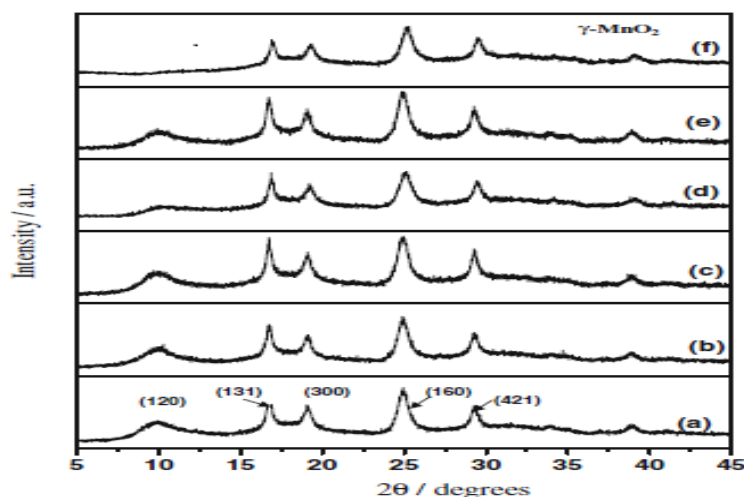


Fig. 5 XRD patterns of EMD (a) No additives (b) 100 ppm Glycine, (c). 100 ppm Sucrose, (d) 100 ppm Saccharine (e) 50 ppm Glycine (f) 50 ppm Sucrose

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 $400\text{--}600 \text{ cm}^{-1}$ confirms the formation of $\gamma\text{-MnO}_2$. The broad peak located at about 760 cm^{-1} was assigned to the characteristic peak of MnO_6 octahedron, while the 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 $\sim 1630 \text{ cm}^{-1}$ was due to O-H bending vibrations associated with the water of crystallization and a broad band at $\sim 3400 \text{ cm}^{-1}$ is due to O-H stretching vibration. A weak band is observed at $\sim 1400 \text{ cm}^{-1}$ 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].

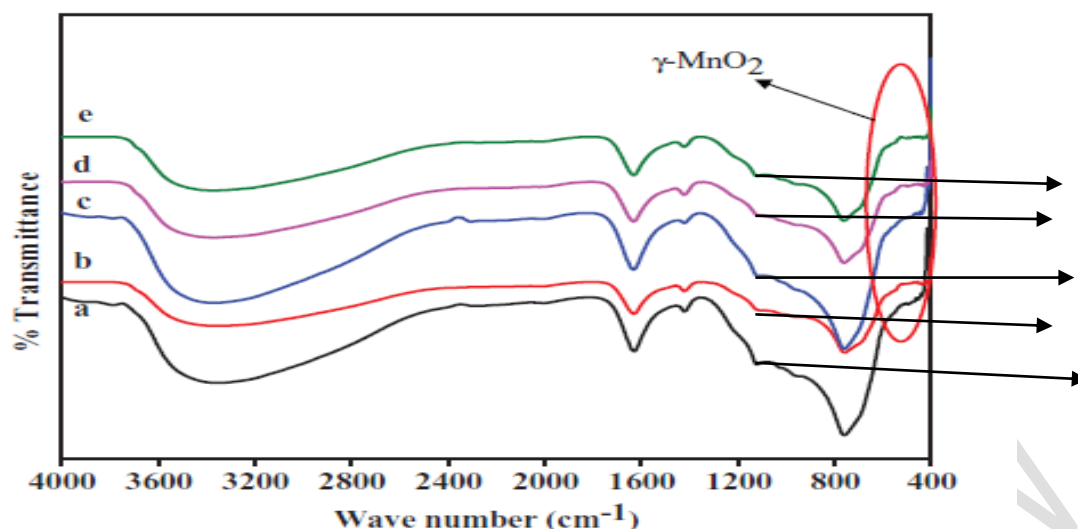


Fig.6:FTIR spectra of EMD(a) No additives, (b) Gly 100 ppm, (c) Sucrose 100ppm, (d) Saccharine 100ppm, and (e) Glycine 50 ppm.

3.4. SEM ANALYSIS:

Morphological changes in deposited material may influence the current efficiency, stability, and rechargeability [8]. Surfactants play significant role on the deposition pattern because of their control on nucleation and growth mechanisms during electrodeposition [29], as well as interactions with the species present in the electrolytic solutions [30]. Organic additives influenced the particle size of the EMD (Fig. 7). Discrete particles with no agglomeration and tiny grain size are detected when 100 ppm Glycine and Sucrose are added (Fig.7 b-c), whereas EMD without additives has a higher grain size (Fig.7 a). This shows that the organic additives resulted in nucleation and current distribution during electrodeposition, thereby enhancing the current efficiencies (CE) of the EMD samples (Table 1). There was a decrease in power consumption during electrodeposition in all cases. However in presence of Saccharine a wider particle size distribution was found.

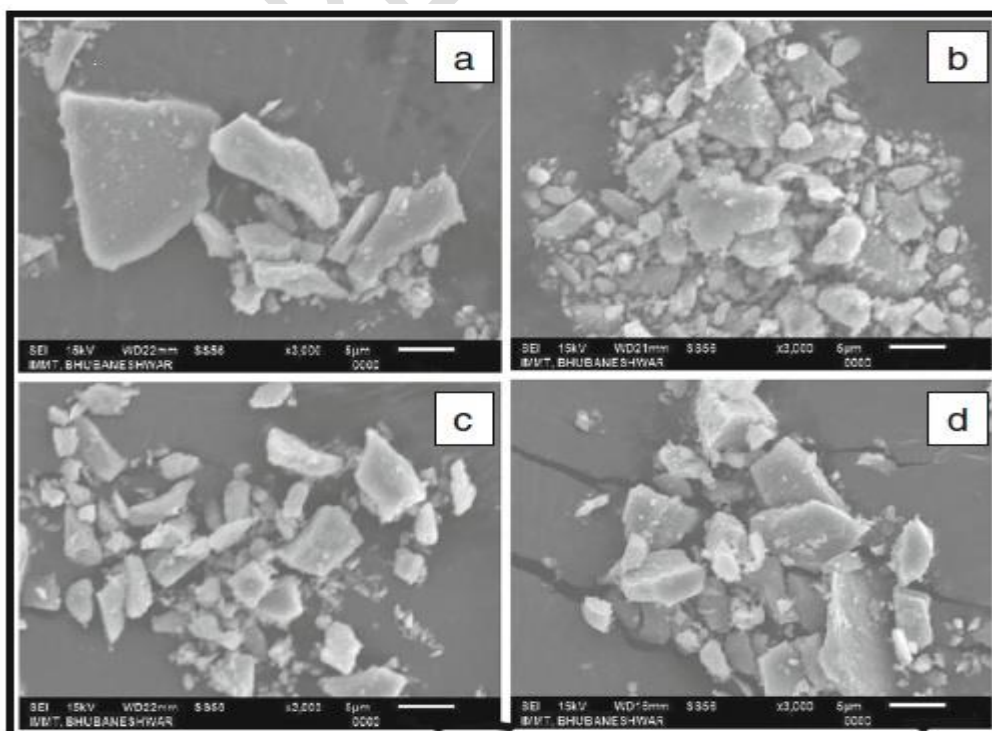


Fig. 7: SEM images of EMD samples prepared from a bath (a) No additives (b) Gly100 ppm (c) Suc100 ppm and (d) Sacch100 ppm

3.5. ELECTROCHEMICAL ACTIVITY:

The electrochemical behavior of the EMD samples was studied by galvanostatic experiments[32]. The charge and discharge characteristics enabled the evaluation of suitability of the prepared EMD as a battery material. The 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:



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 EMD with no additives had a discharge capacity of 240 mAh g^{-1} (870 C g^{-1}), compared to the stated values of 160 mAh g^{-1} (580 C g^{-1}) for EMD without additives [31]. It is interesting to note that the addition of organic additives to the electrolytic cell during MnO_2 electrodeposition had a substantial impact on the discharge performance of the deposited samples. The addition of glycine boosted discharge capacity to 298 mAh g^{-1} . Adding sucrose and saccharine to electrolytic solutions at 100 ppm resulted in 278 and 275 mAh g^{-1} discharge capacities for the EMD. It is also worth noting that the discharge capacity of the EMD produced in the absence of additive decreased very fast (Fig. 8a). However, EMD produced with organic additives maintained discharge capacity for a longer number of cycles (Fig. 8b-d). Adding 10 ppm and 50 ppm glycine (Fig. 9b-c) raised the initial discharge capacity to 285 and 290 mAh g^{-1} , compared to roughly 245 mAh g^{-1} for the EMD without additions. Increasing glycine concentration to 100 ppm (Fig. 9e) resulted in a maximum discharge capacity of 298 mAh g^{-1} . However, raising the concentration of glycine to 250 ppm (Fig. 9d) reduced the discharge capacity to 234 mAh g^{-1} .

Similar behaviour was found for both 10 ppm of sucrose and saccharine (Fig. 10b and 11b), with initial discharge capacities of 259 and 251 mAh g^{-1} respectively. Adding 100 ppm of these additives to the electrolytic solution resulted in initial discharge capacities of 278 and 275 mAh g^{-1} , respectively. However, increasing the concentration to 100 ppm reduced the discharge capacities 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 more stability and discharge capacity.

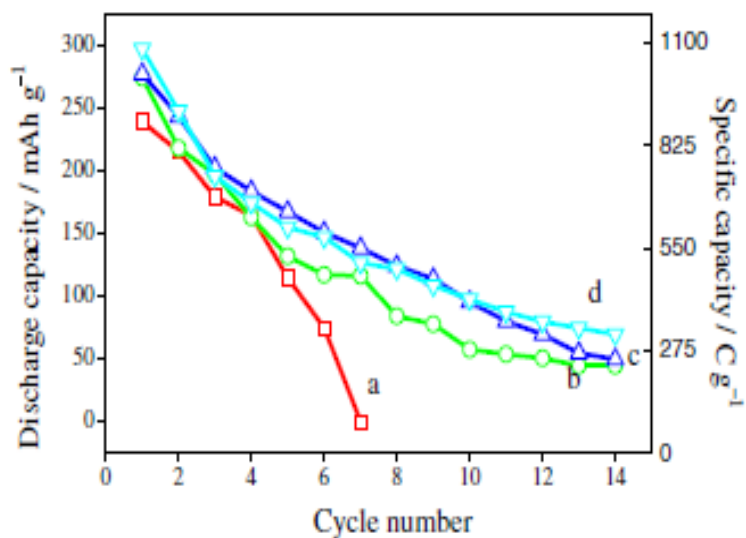


Fig.8: Discharge and specific capacity versus cycling behavior of EMD samples with (a) No additive (b) 100 ppm Saccharine. (c) 100 ppm Sucrose (d) 100 ppm Glycine.

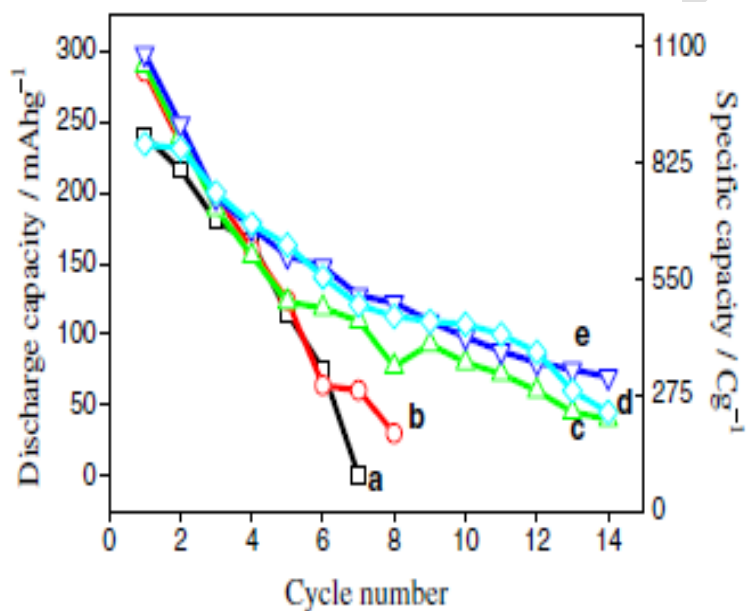


Fig.9: Discharge and specific capacity versus cycling behavior of EMD samples containing Glycine in different concentration. (a) 0 (b) 10 (c) 50 (d) 250 and (e) 100 ppm.

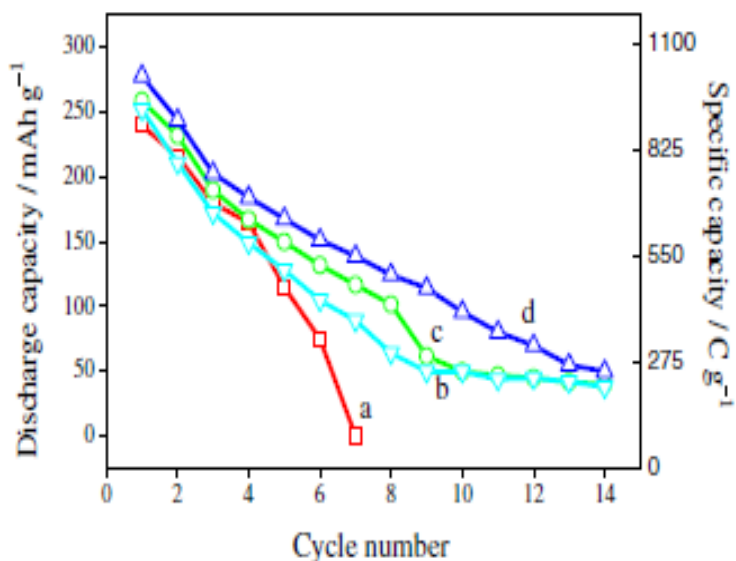


Fig.10: Discharge and specific capacities versus cycling behavior of EMD samples containing sucrose in different concentration (a) 0 (b) 10 (c) 100 and (d) 50 ppm

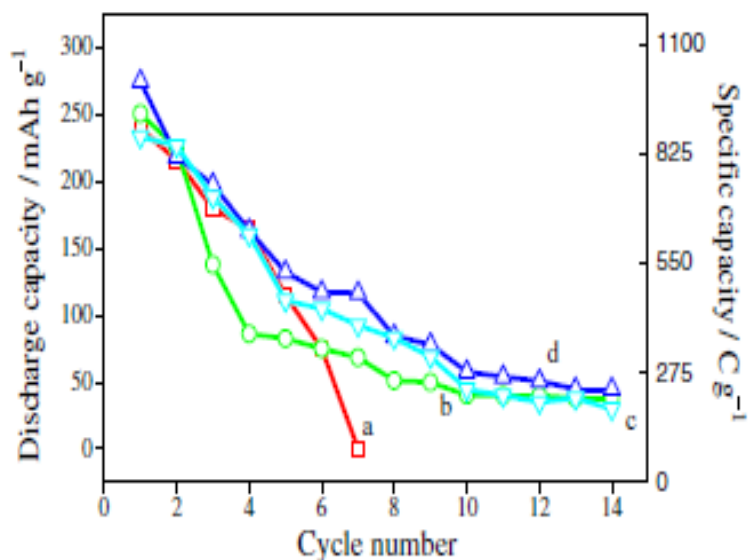


Fig.11: Discharge and specific capacities versus cycling behaviour of EMD samples containing sucrose in different concentration (a) 0 (b) 10 (c) 100 and (d) 50 ppm

4. CONCLUSION

Organic additives played an important role in changing crystal shape, therefore current efficiency and energy consumption are dependent on the type and concentration of additive used. The addition of glycine, sucrose, and saccharine as organic additives during the electrodeposition of MnO₂ did not influence the crystal pattern of the synthesised EMD samples, which all showed the features of γ -MnO₂. However organic additions improve the current efficiency of EMD materials while decreasing the energy consumption of the electrodeposition cell. The organic additives significantly improved the discharge performance of the EMD, increasing the capacity 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 with glycine and sucrose. In the presence of saccharine the value was ~ 275 mAh g⁻¹ (995 Cg⁻¹). The addition of these additives during electrodeposition improved EMD's electrochemical characteristics, and the material produced by these processes has potential for battery applications.

Acknowledgement

The author thanks Dr B.C.Tripathy, Principal Scientist, IMMT, Bhubaneswar, India for his constant support and providing laboratory to carry out this piece of work. The author is also thankful to Ms L. Mohanty for her efforts during the course of carrying out this work.

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