

Scalable Production of Electrolytic Manganese dioxide (EMD) and their Electrochemical Energy Storage in Aqueous Electrolyte

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Abstract: Among the different forms of MnO₂, electrolytic manganese dioxide (EMD) is well-demanded energy storage material suitable for rechargeable batteries and supercapacitors. However, the limitations such as lower capacitance, irreversibility, and cyclability of EMD in comparison with other metal oxides such as cobalt and nickel oxides, have hindered their application in capacitor energy storage. Therefore, in the current work suitable for power sources conferences, we have synthesized scalable EMD from electrolytic baths with varying biopolymer additive concentrations has been investigated for application as an electrochemical supercapacitor. The presence of alginate influenced both the physical and electrochemical storage properties of the electrodeposited MnO₂. At 0.5 g l⁻¹ in the bath, the pristine EMD morphology was rearranged to a cactus-shaped one with flutes. The altered morphology and enhanced particle size are attributed to the ability of the alginate to act as a template for binding the Mn²⁺ ions on the substrate in a relatively ordered and widely distributed manner. The MnO₂ electrowinning plant must consider the effect of electrodeposition parameters that can ensue on the overall impact of electrolytically derived MnO₂ on a larger scale.

Keywords: electrolytic manganese dioxide; aqueous; capacitor; stability; biopolymer, alginate

Introduction

The growing demand for renewable energy sources and the increasing need for grid stability and reliability has led to the development of energy storage technologies. Electrolytic manganese dioxide (EMD) is widely used as a cathode material in batteries and supercapacitors (SC) due to its high electrochemical performance, long cycle life, and low cost. Manganese is also an abundantly available material compared to other transition metal oxides counterparts such as nickel and cobalt oxides which makes it viable. Scalable manganese production is essential for the sustainable development of the global economy, and the efficient use of this critical resource is crucial. The production of manganese by countries must be balanced with the need for environmental protection and social responsibility, ensuring that the benefits of this resource are shared equitably and sustainably. The material MnO₂ exists in different forms of polymorphs which are α -, β -, γ -, λ - and δ - etc. One of the most critical factors affecting EMD's electrochemical performance is its crystal structure. EMD (γ -MnO₂) has a layered structure consisting of MnO₆

octahedra linked together through the edge and corner-sharing, forming tunnels along the c-axis. These tunnels allow for the insertion and removal of lithium ions during charging and discharging cycles. Owing to its excellent electrochemical reactivity compared to other types, γ -MnO₂ has become pre-eminent in energy storage. The higher rate of proton diffusion in the solid phase causes enhanced electrochemical reactivity for delivering high currents at low electrode polarization. The crystal structure and morphology of EMD can be modified through various synthesis methods, such as altering the electrolyte bath concentration while maintaining its pH, to improve its electrochemical performance. Researchers have explored various approaches to synthesize manganese dioxide with varying particle size and morphology, through chemical methods such as template-assisted synthesis, surfactant-assisted synthesis, and microwave-assisted synthesis. The different morphologies with nanostructures show lower diffusion time for electrons and ions compared to the MnO₂ in microstructural morphologies. The EMD has advantages over chemical synthesis due to its low production cost, scalable production, electrochemical activity, and high purity. EMD can be formed from the direct electrolysis of an aqueous electrolytic bath containing manganese sulfate in sulfuric acid. The mode of the electrolysis can be carried out, either way, with potentiostatic or galvanostatic techniques. Galvanostatic synthesis control the reaction rate to provide perfect adherence to the deposit with controlled morphology. Electrodeposition is a simple technique that could be conducted with moderate experimental conditions to tune the material properties such as particle size, density, and morphology, which greatly influence the electrochemical energy storage properties.

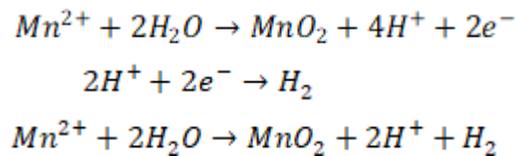
Electrolytic manganese dioxide (EMD) analyzed in most of the previous studies were produced as a self-standing electrode for electrochemical energy storage application, particularly for aqueous batteries and supercapacitors. The self-standing method largely retards the scalability of the material utilized to develop commercial applications. EMD material γ -MnO₂ type synthesized in the present study was deposited in bulk on a lead anode (see Figure 1). In our current study, bulk EMD has been deposited at various current densities of 200-600 A m⁻² and deposition times (4-6 h), and their effects on the microstructure and capacitive behavior were investigated and reported in the presence or absence of additives in the bath. Despite the advantage of producing scalable EMD, the lack of

structural stability for the deposited γ - MnO_2 type results in significant energy storage losses over long-term cycling when used as an electrode in SC applications. Therefore, it is a usual practice, to incorporate metal atom dopants in the bath for improving the surface morphology that enhances the cyclability and stability of the deposited EMD material. To date, different composite electrodes of EMD with metal dopants, polymers, and surfactants have been reported by many researchers. In this work, a unique biopolymer (such as Alginate) as an additive has been made to electrodeposit manganese dioxide from manganese sulfate in a sulphuric acid bath containing the additive. Alginate is an anionic biopolymer that naturally originated from brown algae. This has been extensively used for biomedical applications due to its, biocompatibility, low toxicity, and relatively lower cost. The guluronate (G) blocks (shown in Figure 2) in alginate participate in intermolecular crosslinking in the presence of divalent cations. Therefore, the highly reactive carboxylic acid groups can also be reformed by crosslinking by Mn^{2+} cations. When the alginate reacts with the cation, it makes a cross-linked compound that is not soluble in water. The cross-linking is affected by the affinity which depends on alginate properties, pH, ionic strength, ion radius, steric effects, and electronegativity. Thus, the insoluble polymer can migrate towards the anode and the MnO_2 can adsorb onto the polymer resulting in co-precipitation which will alter the surface morphology in terms of particle size reduction and porosity promotion. Hence it is presumed that the alginate will avoid the dissolution of active material and enhance the stability of the pristine EMD electrode. A range of materials with different levels of additives was electro-deposited and tested to find the trade-off between the amount of the biopolymer and the energy storage capability. The electrodeposited dried mass of EMD (Mn^{4+}) scraped from the anode, followed by thorough washing with de-ionized water, and the sulfate-free product was ground and sieved to obtain the final material.

Experimental

The concentrations of Mn^{2+} and H_2SO_4 used in the electrolytic bath were 0.9 and 0.25 M, respectively. The electrolytic bath used for deposition was a 500 ml glass beaker covered by a machined PTFE lid. 99.99 % pure Pb disk was the anode, and the Stainless Steel 304 disk was the cathode. Prior to conducting the electrodeposition, both electrodes were mechanically polished and, rinsed thoroughly with deionized water to remove extra dust attached to the surface and patted with lint-free tissues. The solution was agitated continuously during the experiment with a Teflon-coated magnetic stirring bar. A set of experiments were carried out under a matrix of conditions such as deposition time period and the current density using the galvanostatic electrodeposition technique. The system was left to react and deposit for 4h, 5h, and 6h time periods, and the current supplied was altered as 100 A. m^{-2} , 200 A. m^{-2}

and 300 A. m^{-2} . For convenience those samples will be denoted as $EMD_{(t,I)}$ where 't' represents the time and 'I' represents the current density. Throughout the experiment, bath temperature was maintained in the range of 90 - 95 °C. The following reactions (Eqs. 1-3) take place in the electrolytic bath during the process.



Soon after the deposition is finished, the Pb electrode was removed from the bath. It was thoroughly rinsed with running deionized water to remove entrained electrolytes. Then it was kept in the oven for drying overnight. The electrodeposited MnO_2 was scraped off the electrode surface cautiously without damaging the electrode to avoid the contamination that occurred by Pb. All pieces were collected and finely ground to get EMD powder. The powdered EMD was rinsed till it completely sweep away the electrolyte attached and dried in the oven at 80 °C overnight. For the Alginate added sample, from a prepared stock solution, the appropriate amount of additive (at different concentrations of Alginate as 0.0, 0.1, 0.25, 0.5, and 1.0 g L^{-1}) was added to the electrolytic bath and stirred constantly. All electrochemical measurements were performed by a potentiostat and EC-Lab software and the battery analyzer. The single electrode cell was constructed with the working electrode, Pt counter electrode, and reference electrode (Hg / HgO) and NaOH 2M aqueous solution was the electrolyte. Manganese dioxide materials were tested within the potential of 0 – 0.6 V for cyclic voltammetry (CV) and charge-discharge (CD) measurements. Various scan rates from 2 to 25 mVs^{-1} were conducted in CV. Current densities from 1 mA to 10 mA were used for CD.

The following equation is used to determine the specific capacitance ($F g^{-1}$) of MnO_2 by charge-discharge data.

$$C_{sp} = \frac{It}{\Delta V m} \quad \text{Eq. (4)}$$

where, I - current rate (A), t - time for discharge (s), ΔV - potential window (V), m - active mass (g). The specific energy density ($Wh kg^{-1}$) and the power density ($W kg^{-1}$) are given by Equation (5) and Equation (6) respectively.

$$E_{sp} = \frac{1/2 C_{sp} (\Delta E)^2}{3.6} \quad \text{Eq. (5)}$$

$$P_{sp} = \frac{E_{sp}}{t} \times 3600 \quad \text{Eq. (6)}$$

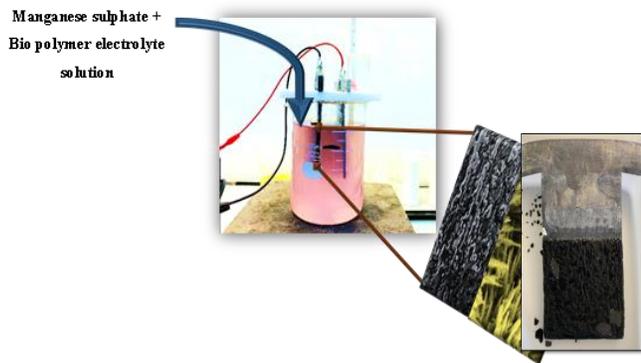


Figure 1 Schematic presentation of the set-up for the electrodeposition of manganese dioxide containing biopolymer additive.

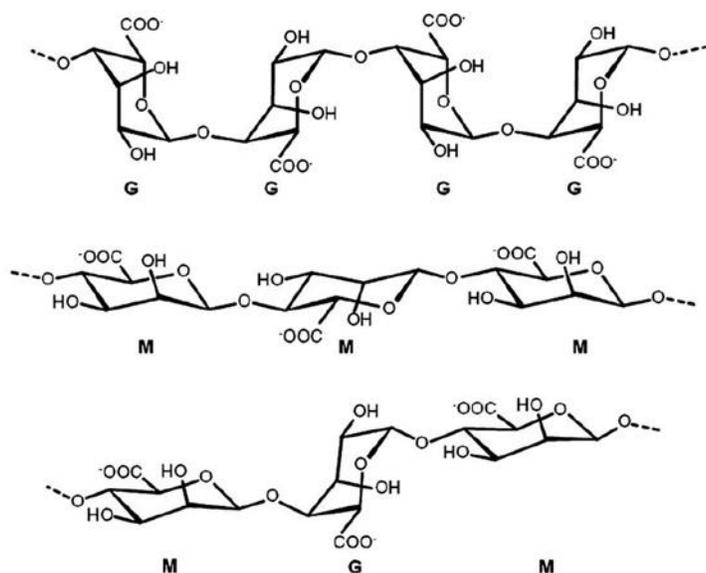


Figure 2 Alginate acid formed by α -L-guluronate (G) and (1,4)-linked β -D-mannuronate (M) blocks.

Results and Discussion

Physical Characterization: The X-ray diffraction (in Figure 3) of the EMD material electrodeposited at different conditions shows the presence of well-resolved peaks of crystalline nature. The FESEM image of the final material show (in Figure 4) improved microstructure and a change in morphology that mainly influenced the higher surface area of the biopolymer samples. The XRD patterns on all EMD have the characteristics of γ form MnO_2 . The X-ray photoelectron spectroscopy (XPS; not shown) of the Mn 2p was fitted with multiplets, all corresponding to Mn^{4+}

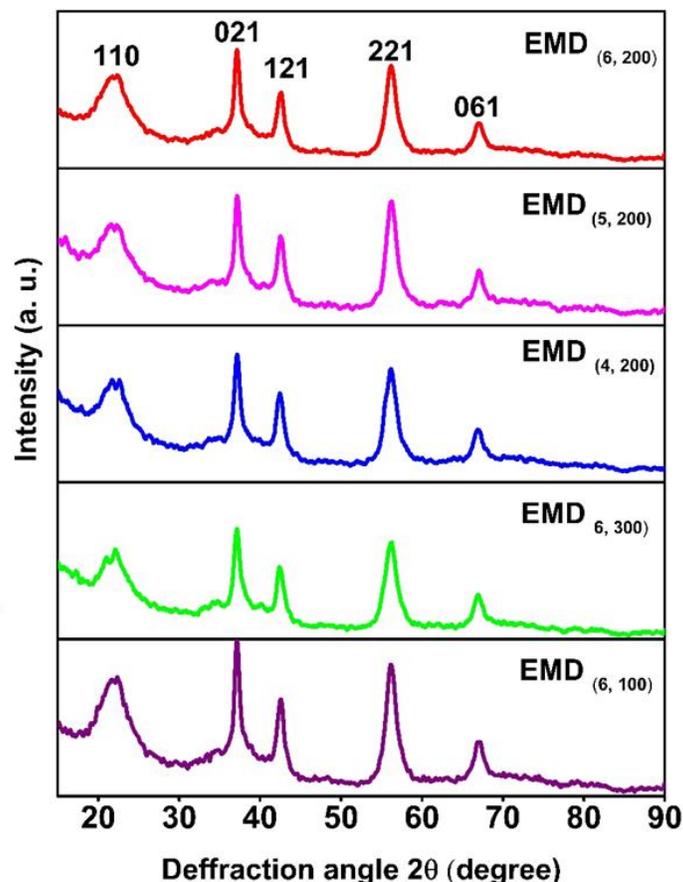


Figure 3 X-ray diffraction patterns of pristine EMD

state. The maximum intensities of the main metal peaks for Mn 2p transitions are found for Mn 2p_{3/2} and Mn 2p_{1/2} at 641.50 eV and 653.38 eV respectively. The increase in the thickness and elongation of the needle-like spines of the cactus-shaped (Figure 4b) particle indicates that the biopolymer is crosslinked onto the surface layer of electrodeposited MnO_2 . The synthesis of EMD through an electrodeposition process within situ addition of a biopolymer in an electrolytic bath is reported here for the first time with an emphasis to enhance the cycling stability of battery and supercapacitor applications.

Electrochemical characterization: For electrochemical single-electrode studies, EMD served as a cathode. The cathode consisted of an active material made of EMD, mixed with acetylene black and binder in the presence of a solvent. The slurry was then coated on a graphite sheet of 1 cm² as substrate and dried at 60 °C for 1h. A biopolymer additive exhibited well-defined quasi-rectangular CV curves (compare Figures 5a & b) and better discharge time (five times larger) upon various current rates corresponding to the pseudocapacitive nature of the biopolymer samples. However, the pristine EMD showed its elliptical CV curves (Fig. 5a) and non-symmetrical charge-discharge curves (compare Figure 5b)

&d). At higher scan rates, the shape of the CV curve deviates from quasi-rectangular to elliptical, indicating the deviation from ideal capacitive behavior. Since the EMD described in this work is less crystalline, it tends to follow the surface adsorption/desorption mechanism through the microporous structure allowing the transportation of electrons and ions. The galvanostatic charge-discharge (GCD) tested at a constant current density of 1 mA cm^{-2} delivered enhanced specific capacitance of 487 F g^{-1} for biopolymer-assisted EMD which is about five times that of the pristine EMD. Adding the biopolymer to the electrolytic bath, grafted the EMD molecules onto the anode substrate. The role of biopolymer in the electrolytic bath is shown to be not limited to the material stability but also paving the path for efficient production of EMD. For practical applications, an asymmetric device comprising a two-electrode system has been fabricated (not shown here) using biopolymer-assisted EMD as positive and activated carbon (AC) as negative electrodes delivering a specific capacitance of 52 F g^{-1} having an energy density of 15 Wh kg^{-1} . In terms of Zn-MnO_2 (EMD) battery

applications, the obtained initial capacity is 275 mA h g^{-1} and after multiple (50) cycles 75 mA h g^{-1} of the discharge capacity is retained.

Conclusions

The EMD was deposited on the Pb anode via Mn^{2+} oxidation to form Mn^{4+} and its oxide MnO_2 . The physicochemical and electrochemical characterization of the obtained EMD powder concluded that the material deposited at 200 A m^{-2} for 5 hours, showing the spindle-like morphology was suitable over others for supercapacitor (SC) application. At 2 mA cm^{-2} , the fabricated hybrid capacitor comprising EMD versus Activated Carbon delivered 52 F g^{-1} specific capacitance, 14 Wh g^{-1} specific energy, 500 W g^{-1} specific power, and 94 % capacitance retention over 5000 cycles. The results highlighted the importance of the functional molecular structure of the biopolymer alginate to produce a binary composite of EMD-polymer as a capacitor material. Improving scientific understanding of the anodic electrodeposition of MnO_2 represents an opportunity to guide the electrowinning plant for scalable and economic production.

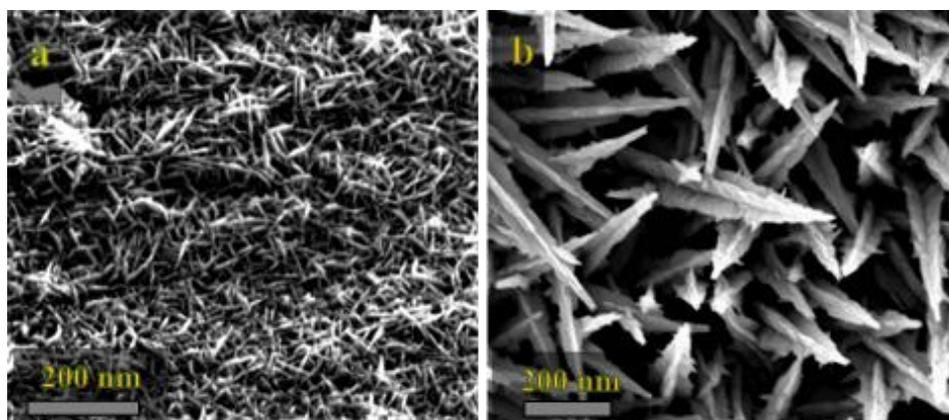


Figure 4 FESEM images showing the change in morphology of the final material (a) pristine EMD; and (b) biopolymer assisted EMD.

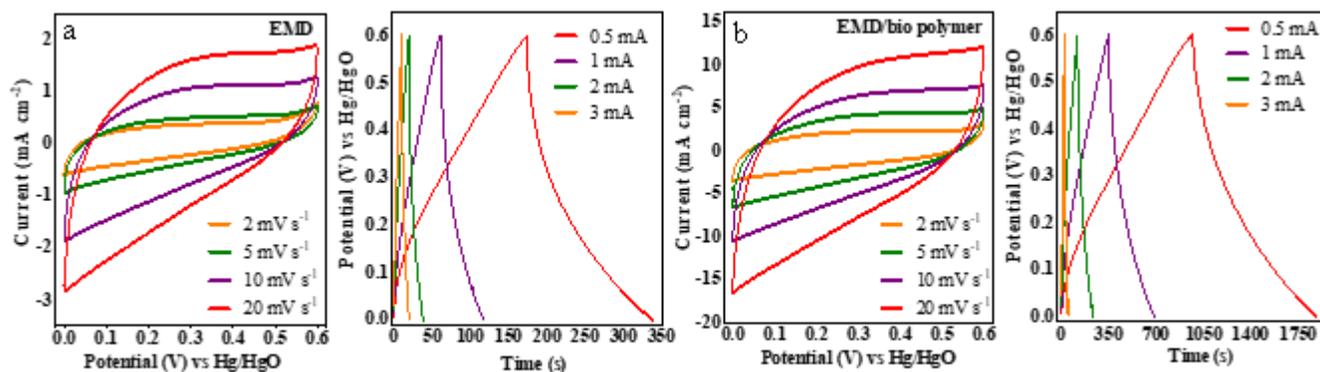


Figure 5 Cyclic voltammogram (CV) and galvanostatic charge-discharge (GCD) curves of a single electrode study (a) pristine EMD materials, (b) biopolymer assisted EMD (0.5 g L^{-1}), respectively conducted in 2M NaOH aqueous electrolyte .