

Redox Deposition of Manganese Oxide Nanoparticles on Graphite Electrode by Immersion Technique for Electrochemical Super Capacitors

Ann Tresa George*, R. Ganesan and T. Thangeeswari

Department of Physics, Vel Tech Multitech, Avadi, Chennai - 600 062, Tamil Nadu, India;
anntresageorge@veltechmultitech.org, ganesan@veltechmultitech.org, thangs.ok@gmail.com

Abstract

Objectives: To fabricate the electro chemical; super capacitors by single step control redox deposition process for coating manganese oxide onto the surface of a graphite cylindrical electrode. The purpose of this investigation is to employ manganese oxide as the electrode material along with a graphite electrode due to its low cost, environmental benignity and excellent capacitive performance in aqueous electrolytes. Manganese oxide is a very catching material compared to ruthenium oxide materials due to its availability, low cost and non polluting effects. **Methods:** The sample is prepared by the immersion technique by varying the immersion time of the graphite electrode with analytical grade Potassium permanganate, Sulphuric acid, Hydrochloric acid and Acetone as precursor sources. Double distilled water was used throughout the experiment. Epoxy resin was used to give the insulating coating for the graphite rod to make a graphite electrode. **Statistical Analysis:** The Energy Dispersive X-ray (EDAX) analysis gives the amount of oxygen, manganese and carbon present in the sample. The morphology of the manganese oxide coating on the graphite electrode was observed using Scanning Electron Microscope (SEM). Cyclic voltammograms, and chronopotentiometric charge-discharge analysis were taken. **Findings:** From the cyclic voltammogram measurements we can concluded that the manganese oxide coated graphite electrode has high operational stability. The chronopotentiometric charge-discharge curves demonstrate high electrochemical reversibility and good stability. Scanning electron microscope results demonstrates that the agglomeration of particles is less. The observed spherical particles are between 220 and 415 nm in diameter. **Applications:** The most successful and practical process used for electrochemical energy conversion and energy storage are batteries, fuel cells and Electrochemical Supercapacitors (ES). In recent research, ES have attracted considerable attention, mainly due to its high power density, long life cycle and bridging function for the power and energy gap between established dielectric capacitors (which have high power output) and batteries and fuel cells.

Keywords: Electrochemical Supercapacitors, Electrodes, Graphite, Redox Deposition, SEM

1. Introduction

In the fast development of the global economy, the depletion of fossil fuels, rise in environment pollution, growing human population along with the raise in energy demand, the global energy consumption has been accelerating at an shocking rate. At current

utilization rate, global energy exhaustion will become inevitable¹. Owing to a tremendously increasing energy consumption of modern societies, the development of sustainable and renewable energy sources is becoming one of the most important fields of research. There is an burning need for efficient, clean and sustainable source of energy. Green energy sources like solar and wind

*Author for correspondence

energies are intermittent due to its energy harvesting may be interrupted during night or in places where wind does not blow. Hence it is more important to develop high-performance, low cost and environmental friendly energy conversion and storage systems. Furthermore, the most effective and practical process for electrochemical energy conversion and to store the energies are batteries, fuel cells and Electrochemical Supercapacitors (ES). In past research years, ES have drastic attention mainly due to their high power density, long life cycle and bridging function for the power and energy gap between traditional dielectric capacitors (which have high power output) and batteries and fuel cells (which have high energy storage)². Thus it can be used in much wider array of fields such as backup or alternate power source, hybrid electric vehicle, engine starting system and telecommunication.

Among the various electrode fabricating methods for supercapacitors, the drop-drying method, spray deposition and Meyer rod coating deploy the working materials loosely onto the metal current collector which resulting in electrodes with very high internal resistance due to poor contact between the working media and the metal current collector³. The remaining techniques such as electrophoretic deposition, electrostatic spray deposition and layer-by-layer assembly, while improving the internal binding and hence producing the electrodes with very small resistance and excellent response can only incorporate limited active materials into the electrodes. As a result, the supercapacitors which prepared by above mentioned methods can not store sufficient electricity for various practical applications. Although, certain factors that have to be consider while fabricating a supercapacitor such as energy density (usage life after one charge) and power density (rate of discharge). These factors are the main drawbacks for supercapacitors when being considered for more power demanding device applications³.

The main challenge therefore was to find a way to fabricate a technique which not only prepares electrodes with good electrochemical response but also a satisfactory power storage capability. Metal oxides with various valance states are gaining interest in the preparation of electrodes. Ruthenium oxide is among these materials that show the best properties for the preparation of the electrodes but it has high cost, availability is less and the polluting effect on the environment makes this material repellent for large scale use. On the other hand, manganese oxide

is a material with more attention towards research for its availability, low cost and non polluting effects compared to ruthenium oxide⁴. Due to this reasons, in recent research the manganese oxide material is extremely studied in order to attain more acquaintance about its properties and to find relations between morphological, structural, compositional characteristics of the material with the electrochemical performance of supercapacitor based on this material⁴.

This research work explains about a single step and controllable redox deposition method for coating manganese oxide on the surface of a graphite cylindrical electrode by the immersion technique⁵.

2. Experimental

Analytical Grade Potassium permanganate, Sulphuric acid, Hydrochloric acid and Acetone were used as received material without any further purification. Double distilled water was used throughout the experiment. Epoxy resin was used to give the insulating coating for the graphite rod to make a graphite electrode. All electrochemical observations were carried out at room temperature. A graphite rod was used as a substrate due to its higher specific surface area (higher than that of carbon nano tubes), lower specific resistance (lower than that of activated carbons) and a higher percentage of mesopore size distribution (higher than that of activated carbon)⁶. For this experiment the required graphite rod was obtained from a dry cell battery as shown in Figure 1, the rod was cleaned thoroughly for the experiment. The graphite rod obtained from the dry cell battery had a diameter of 8 mm and a length of 5.8 cm. The obtained graphite rod for this experiment is shown in Figure 2. The thus obtained graphite rod was cleaned for it to be used for the experiment. Figure 3 shows a flow chart of the cleaning process of the obtained graphite rod. Now after the oven drying process the graphite rod was encapsulated with Epoxy Resin to make the graphite electrode which is the substrate in this experiment. Epoxy otherwise known as polyepoxide is a thermosetting polymer produced from reaction of an epoxide 'resin' with polyamine 'hardener'. One end of the electrode was unchained of epoxy resin for electrical connection and the other was abraded with Silicon Carbide (SiC) paper for immersion. Figure 4 shows the graphite electrode obtained with epoxy resin insulation and electric connection; this was used for the fabrication of the super capacitor.

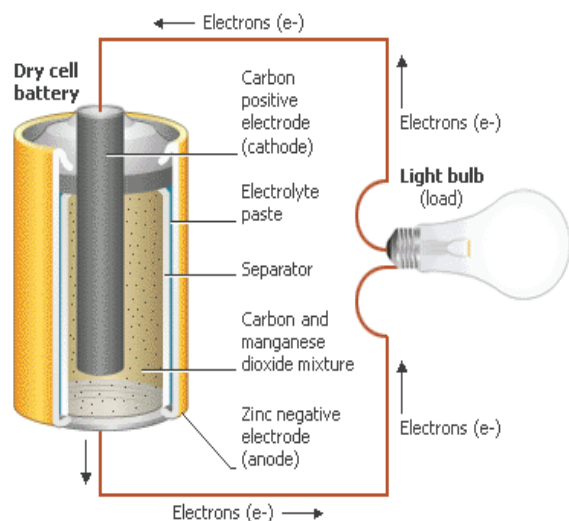


Figure 1. Graphite rod from the Dry cell battery.



Figure 2. Graphite rod.

Metal oxides with various valence states are acquiring growing interest in the preparation of electrodes with pseudo capacitive properties for super capacitor applications¹⁴. Manganese oxide is a material very attractive for its high availability, low cost and non-polluting effects. They have attracted considerable research interest due to their distinctive physical and chemical properties and applications^{7,16}.

The capacitance of manganese oxide material is predominantly due to pseudo capacitance, which is attributed to reversible redox transitions involving exchange of protons and/or cations with the electrolyte⁸.

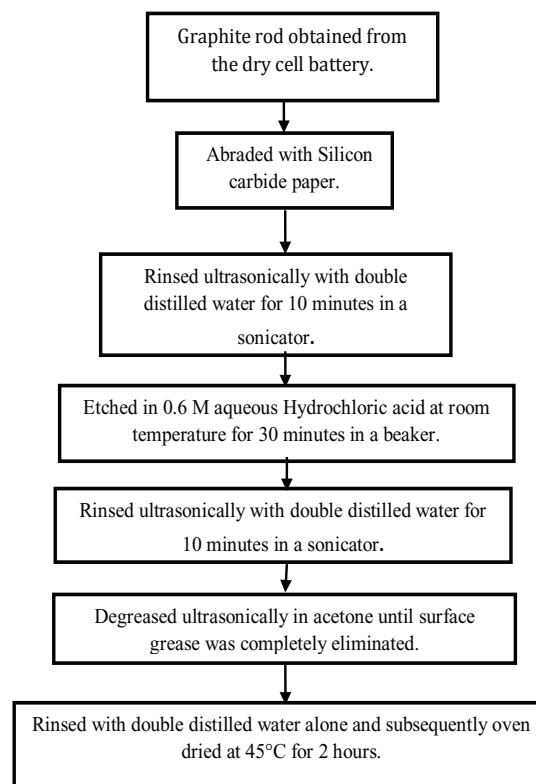


Figure 3. Flow chart of the cleaning process of the graphite rod.



Figure 4. Graphite electrode with epoxy coating and electric connection.

In this research work, we synthesized a single-step and controllable Redox deposition process for coating manganese oxide on the surface of a graphite electrode by the method of immersion. The immersion solution for the redox deposition was prepared by using double distilled water and reagent grade chemicals by mixing 80 mL of 0.25 M KMnO_4 (Potassium permanganate) with 20 mL of 2.5 M H_2SO_4 (sulphuric acid). The fabricated graphite electrode was placed up and down in a beaker containing the newly prepared $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ solution, which

was continuously stirred during the deposition⁹. The deposition process were carried out at room temperature for the duration of 60 minutes and 80 minutes. The manganese oxide electrode was then rinsed with double distilled water and subsequently oven dried at 50°C in air.

3. Results and Discussion

The redox deposition of manganese oxide on the prepared graphite electrode was done by the immersion technique. The deposition was carried out for 60 minutes and 80 minutes of immersion time in identical but aqueous solutions containing 0.25 M of KMnO_4 and 0.5 M of H_2SO_4 . During immersion of the electrode in the stirred solution, very slight change could be seen on the electrode surface. However, during removal of the electrode from the solution, a coating was visible on the electrode¹⁰. The mass of the electrode before and after the deposition was not measured, but it is expected that the mass of the coating should increase with the deposition duration.

3.1 Scanning Electron Microscopy (SEM)

The surface morphology of the electrode prepared by the immersion technique was studied using SEM imaging techniques. Typical micrograph of the as-deposited coating after 80 minutes deposition is shown in Figure 5. Distinct morphology of the particles became difficult to be seen from that image. For better visibility of the particles SEM images in 5 μm level was taken as in Figure 6. This image shows a predominant morphology of almost spherical particles or many small spherical grains¹¹.

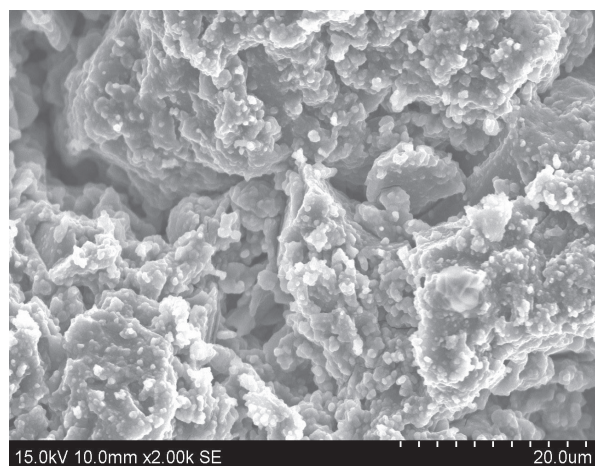


Figure 5. SEM image of the surface of graphite electrode after 80 min of immersion time with magnification of 20.0 μm .

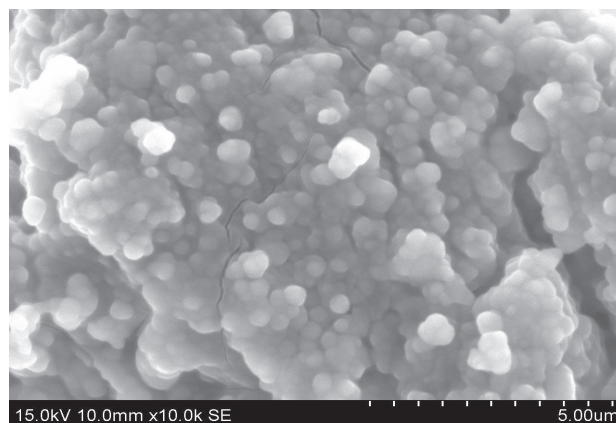


Figure 6. SEM image of the surface of graphite electrode after 80 min of immersion time with magnification of 5.00 μm .

Porosity is of great importance in the performance of supercapacitor electrodes. The charge-discharge mechanism involves adsorption-desorption of ions. Therefore efficient ion transport from solution to the active material in pores is necessary in order to achieve a high SC. Moreover, the transport of ions in the pores is essential in order to reduce the electrical resistance of the electrodes. Agglomeration of the particles is less in the images. The observed spherical particles are size between 220 and 415 nm in diameter as in Figure 7.

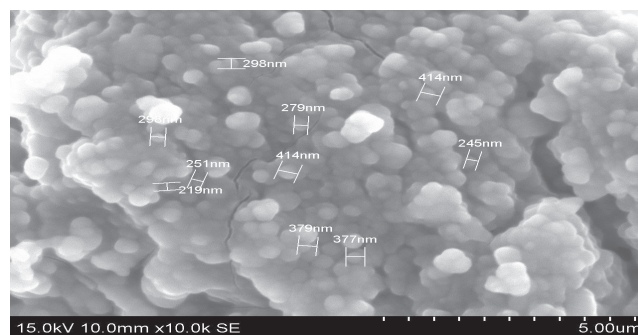


Figure 7. SEM image showing the diameter of the deposited particles.

The images show that there is a coating of the material on to the cleaned graphite electrode surface due to the deposition by immersion technique.

3.2 Energy Dispersive X-ray Spectroscopy (EDS)

The chemical composition of the coating, that the graphite electrode got by the immersion technique, was analyzed

by the energy dispersive X-ray spectroscopy. Taking the EDS of the prepared sample, spectrum confirmed that the as-prepared electrode consisted of Mn and O and C elements as in Figure 8.

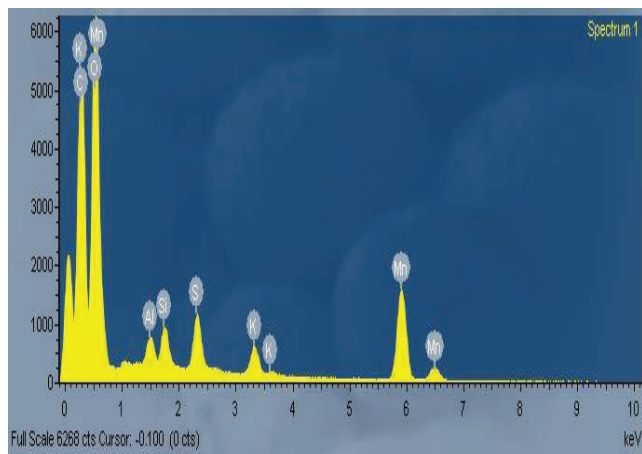
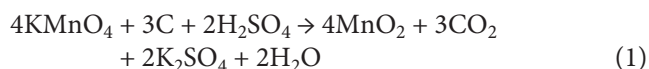


Figure 8. Energy-dispersive spectroscopy of the electrode surface.

The EDS of manganese oxide coated graphite electrode surface shows the molar ratio of Mn and O as 11.10: 35.46, and for C is 49.25. It is known that in an acidic permanganate solution, carbon can be oxidized and the products include manganese (IV) oxide and carbon dioxide. Using thermodynamic data, one can derive the following reaction given by Equation 1



This reaction shows the redox deposition of manganese oxide onto the graphite electrode. It should be noted that the formation of CO_2 gas was not noticeable during the period of electrode immersion. This was very likely due to the dark-purple color of the solution and also the continuous stirring process of the solution.

3.3 Electrochemical Studies

3.3.1 Cyclic Voltammogram (CV)

The electrochemical properties of the prepared electrode have been investigated using cyclic voltammetry between the potential ranges of -1.0 to 0.4 V, at a range of scan rates between 10 mV/s to 40 mV/s in 1 M Potassium chloride solution. Figure 9 and Figure 10 shows the cyclic voltammograms of manganese oxide electrodes at 60 and 80 minutes immersion time respectively. As we know,

the shape of the CV loops of a supercapacitor should be rectangular provided that there is a low contact resistance and larger resistance distorts the loop¹². Within the potential range the shape of the CV curves reveals that the capacitance characteristic of the given electrode samples is typical pseudo capacitance which is totally different from the electric double-layer capacitance, which would produce a CV curve close to an ideal rectangular shape. The specific surface area of the electrode material is a key factor restricting its double layer capacitance. The faradic pseudo capacitance is 10–100 times or much higher than that of the double-layer capacitance, and the charge/discharge processes are not only limited to the adsorption/desorption in two-dimensional surfaces, but also can be three-dimensional intercalation or redox reactions of ions to produce pseudo capacitance.

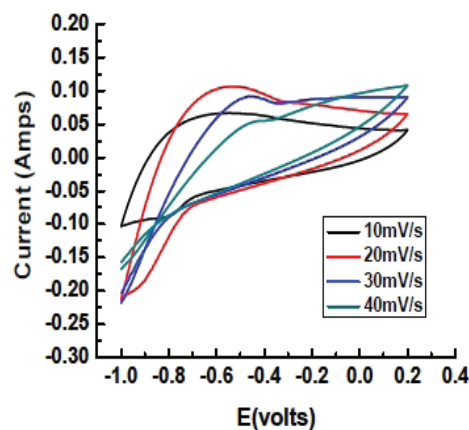


Figure 9. CV curve of the manganese oxide electrode immersed for 60 minutes.

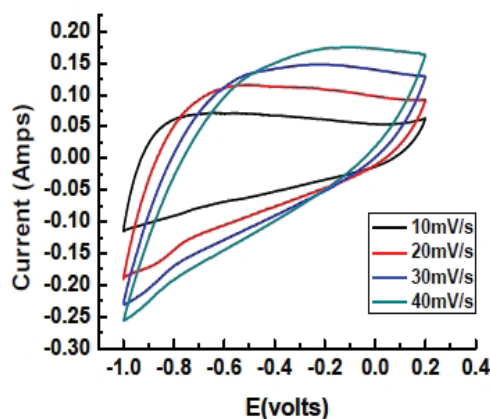


Figure 10. CV curve of the manganese oxide electrode immersed for 80 minutes.

At any given scan rate, the higher the immersion time, the capacitance value is high, but with in the value of 100 m V/s. The reason for the above mentioned is may be that the higher the immersion time, the more the amount of immersed manganese oxide and the more numerous the potentially electro active sites, thus leading to higher capacitance. However, if the manganese oxide is too compact for the electrolyte ions not to easily diffuse into the inner layers of the immersed graphite electrode, then some active sites on inner layers are not able to contribute to capacitance at longer immersion times¹³.

The diffusion layer above the electrode surface will be different for various voltage scan rate used. In a slow voltage scan, the diffusion layer will grow more from the electrode in comparison to a fast scan. Consequently the reactant flux to the electrode surface is considerably smaller at slow scan rates than at faster rates. With increase in scan rates, the anodic and cathodic peaks are shifts towards higher and lower potential respectively. At higher voltage scan rates, the two reduction peaks merges together and becomes less distinctive. Again, the positive sweeps of CV curves are not symmetric to their corresponding negative sweeps which concludes the kinetic irreversibility in the redox process due to polarization and Ohmic resistance during the Faradaic process occurring in the prepared electrode. Capacitive nature of MnO coated graphite electrode is identified from the CV curve shown in the above figures. The capacitive nature is assumed to be in between pseudocapacitive and rectangular double layer capacitive nature.

3.3.2 Chronopotentiogram

The charge/discharge characteristic of the manganese oxide coated graphite electrode or the manganese oxide electrode was studied using Chronopotentiogram (CP). The current density is kept constant at 1 mA and variation of potential with respect to time is studied. Figure 11 and 12 shows the charge/discharge plot for the as-prepared electrode immersed for 60 minutes and 80 minutes respectively, in the potential range of 0.0 to 0.8 V.

From Figure 11 and Figure 12 we can see the charge and discharge curves for the 1st to 20th charge discharge cycle are symmetric and similar isosceles triangles. This demonstrates that the prepared graphite electrode has high electrochemical reversibility and good stability¹⁶⁻¹⁸.

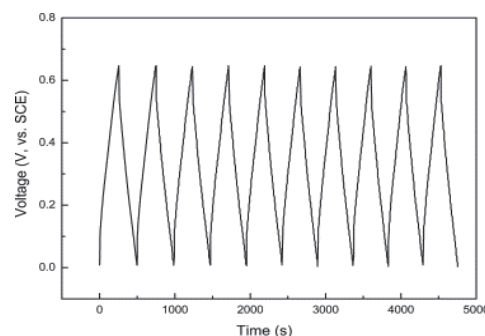


Figure 11. Charge/discharge plots of MnO electrode immersed for 60 minutes.

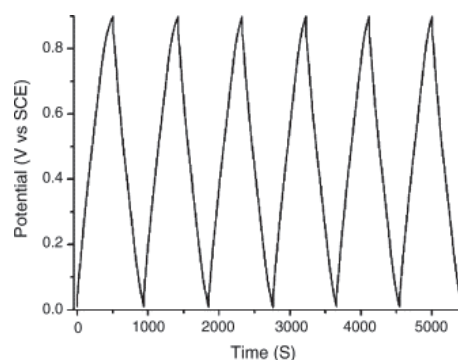


Figure 12. Charge/discharge plots of MnO electrode immersed for 80 minutes.

From all the above results and discussions we can concluded that the redox deposition of manganese oxide on graphite electrode by immersion technique for varied immersion time of 60 and 80 minutes exhibits ideal capacitive behavior for the application of electrochemical supercapacitors.

4. Conclusion

Manganese oxide coated graphite electrode was prepared using a simple, fast and controllable redox deposition by immersion technique. The capacitive behavior of the prepared electrode was analyzed by varying the immersion time of the electrode. The surface morphological changes of the prepared electrode was examined using SEM microscopic techniques. In SEM images were able to show the spherical morphology of the coated electrode surface. The chemical composition of the coating in the electrode surface was studied by energy dispersive X-ray analysis technique. The cyclic voltammetry of coated electrodes in a neutral aqueous solution exhibited characteristic capacitive behavior. The Chronopotentiometry charge/

discharge curves demonstrates the electrochemical stability of the prepared electrode. This research results are very interesting in the perspective of practical application of manganese oxide in supercapacitors.

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