SOLID STATE PROPERTIES AND APPLICATIONS OF MNO_2

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SOLID STATE PROPERTIES AND APPLICATIONS OF MNO_2

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DECLARATION

I hereby declare that the work embodied in this report entitled "SOLID STATE PROPERTIES AND APPLICATIONS OF MNO_2" was carried out by me during the year 2021-2022 under the guidance of Dr. Shrikant Naik. In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

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SAIRAJ SURYAKANT NAIK

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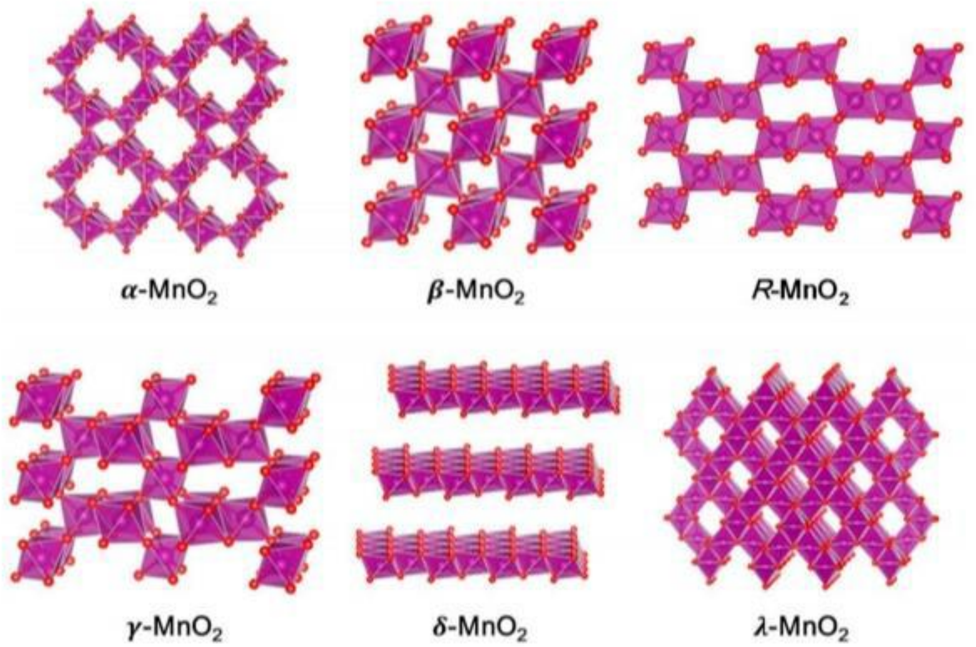
INTRODUCTION

MnO2 is a component of dry cell batteries. It acts as an inorganic pigment in ceramics and in glassmaking. It can also be used as oxidant in organic synthesis.
There are altogether six polymorphs of manganese dioxide which include:

1. α- MnO2 (hollandite)
2. β- MnO2 (pyrolusite)
3. R-MnO2 (Ramsdellite)
4. γ- MnO2 (nsutite)
5. δ- MnO2 (birnessite)
6. λ- MnO2 (spinel)



Manganese (IV) oxide is the inorganic compound with the formula MnO_2. This blackish or brown solid occurs naturally as the mineral pyrolusite, which is the main ore of Manganese and a component of Manganese nodules.

In the last decade, synthesis and characterization of manganese oxides in various oxidation states and/or different structures have been intensified due to their promising potential for application in various fields such as catalysis, secondary batteries and supercapacitors, paints, coloured glass, fertilizers, etc.

Manganese dioxides are of considerable interest due to their high applicability in various fields. Because of high-specific capacitance, high-energy density, environmental friendliness, and natural abundance, manganese dioxides have been extensively studied as active electrode materials for electrochemical capacitors.

Several polymorphs of MnO_2 are claimed, as well as a hydrated form. Like many other dioxides, MnO_2 crystallizes in the rutile crystal structure (this polymorph is called β-MnO_2). The coordination number of the cation is 6 and that of the anion is 3, i.e. 6 anions are arranged approximately octahedrally about the cation and 3 cations trigonally about the anion.

MnO_2 is characteristically nonstoichiometric, being deficient in oxygen. The alpha-polymorph of MnO_2 has a very open structure with "channels" which can accommodate metal atoms such as silver or barium. α- MnO_2 is often called Hollandite, after a closely related mineral. MnO_2 in a polymorph can incorporate a variety of atoms (as well as water molecules) in the "tunnels" or "channels" between the manganese oxide octahedra. There is considerable interest in α-MnO_2 as a possible cathode for lithium ion batteries.

In addition to the dioxide which occurs naturally as pyrolusite there are many materials which have either been prepared in the laboratory or have been found in the material world with compositions approximating to MnO_2. MnO_2 is widely used as a depolarizer in Leclanche type dry cell. Only gamma forms of Mn oxides are suitable for use in battery and these either comes from ores e.g. ramsdellite ore are produced chemically or electrolytically. The principal use for MnO_2 is for dry-cell batteries, such as the alkaline battery and the zinc carbon battery. Manganese dioxide is reduced to the manganese oxide hydroxide MnO(OH) during discharging, preventing the formation of hydrogen at the anode of the battery. Thereby polarization in dry cells (primary cells) is corrected by Manganese (IV) oxide MnO_2.

Newer alkaline batteries (usually battery cells), use the same basic reaction, but a different electrolyte mixture.

There has been a phenomenal rise over the years in the consumption of manganese dioxides for use as the active cathode material in MnO_2 based dry cells. Rechargeability of the MnO_2 cathode has greatly increased its industrial potential. In this review the electrochemistry of the dioxides is discussed with special emphasis on recent developments in the field, in particular the solid state properties. [1]

LITERATURE REVIEW

1) Solid state properties

A) Electrical conductivity

Pellets of MnO_2 powder are difficult to form and conductivity studies are usually done within the press-tool. Manganese dioxide is known to be a semiconductor with specific conductivities ranging from 10^{-6} to 10^{3} $(\Omega\ cm)^{-1}$.[2]

Bhide and Damle [3] investigated the properties of naturally occurring pyrolusite from various sources, some of these samples being massive and possessing crystal orientation. They studied both d.c. and a.c. conductivities and observed an anomaly in the dielectric constant of the samples at about 50˚C. This was documented to its ferroelectric behaviour and was discussed in relation to its crystal structure. Certain manganese minerals show a decreased conductivity in the order pyrolusite > psilomelane > manganite.

Electrical conductivity measurements of manganese dioxides are important both from the point of view of fundamental structural investigations and electrochemical behaviour. There seems to be a general consensus that the manganese dioxide is a mixed conductor wherein both electrons and holes participate in the conduction mechanism [4,5]. The band structure of the dioxide, however, is not well understood and, therefore, it has not been possible to correlate the activation energy and the band gap. It would also be interesting to conduct thermal e.m.f. studies which could throw light on the nature of the second-order transition (para- to antiferromagnetic) between 76 and 84 K. There also exist close correlations between the powder conductivity, thermal behaviour, water content and electrode potential. Hence, there is a need for further investigation in this field.

B) Magnetic Properties

On the basis of magnetic susceptibility measurements of the cathodic reduction products of MnO_2 at various stages of discharge, following are the successive stages through which the reduction proceeds: γ-MnO_2 → lattice dilation →γ-Mn_2O_3 → MnOOH →Mn_3O_4. Similar studies were earlier reported but the interpretation, that MnO_2 reduces to Mn_2O_3, was found to be untenable. It is believed that even very subtle structural variations, such as those indicated by changing intensities of particular X-ray diffraction peaks, could affect the magnetic susceptibilities of manganese dioxides. [6]

C) Infrared Spectroscopic Studies

High resolution infrared spectral measurements carried out by Potter and Rossman [7] provided information on the structure and H_2O content of various Mn(IV) oxide phases. The presence of bound water in ramsdellites was clearly observed in their spectra. Spectra of heat-treated nsutites indicated possible concentrations of randomly distributed pyrolusite domains with rising temperature. These studies also showed that:

(a) birnessite has a layer structure,

(b) synthetic buserites and birnessites have analogous layer structures,

(c) the shift from the 10 Å to 7 Å spacing in the X-ray diffraction is caused by water loss rather than by a structural rearrangement of the [MnO_6] framework, and
(d) natural todorokite is a valid mineral (not a mixture of buserite and its decomposition products birnessite and manganite).

D) Electrochemical Properties Of MnO_2

Manganese dioxides are extensively used as active cathode materials in Leclanche or alkaline Zn/MnO_2 cells. The nature of the cell reaction depends on the nature of the electrolyte and also on the discharge conditions [8]. Kozawa and Powers [9] suggested that the cathodic reduction takes place by the incorporation of protons and electrons into the MnO_2 lattice: $MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^-$
A manganese dioxide which gives maximum energy with as high a cell voltage as possible is the most electrochemically active [10]. Many physical and chemical properties such as electrical conductivity, porosity, MnO_2 content, surface area, electrode potential, etc. have been measured and discussed in terms of dry cell performance. The combination of these factors which renders a given sample of MnO_2 most active, however, has been in question for years [11]. Brenet and co-workers in 1975 [12] were amongst the earliest to attempt any meaningful correlations between these factors. They established the importance of a large number of pores with mean radii between 15 and 24 Å as well as the existence of large amounts of OH groups in highly active dioxides. Activity of MnO_2 is determined by the type of OH groups present and the mobility of oxygen in the MnO_2 lattice. Voinov [13] explained the relative superiority of the γ-manganese dioxides compared to the α and β forms on the basis of the proton insertion in the tetrahedral sites of the hexagonal close-packed oxygen layers. The presence of some of the tetrahedra which share no faces with the octahedra in a diaspore-type structure (γ-MnO_2, ramsdellite) was believed to favour proton diffusion (from the tetrahedral site to the other via an intermediate octahedral site). This effect is reinforced by lattice distortions which occur in a diaspore-type structure.

2) *Applications Of MnO_2*

A) Sol-gel MnO_2 as an electrode material for electrochemical capacitors

MnO_2 was synthesized by the sol–gel method. Two forms of MnO_2, namely xerogel and ambigel, were prepared by reduction of $NaMnO_4$ and KMnO4 with sodium fumarate. The synthesized products were characterized using X-ray diffraction (XRD), Brunauer–Emmet–Teller (BET), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and chemical analysis. Electrochemical characterization was carried out using cyclic voltammetry by a three electrode system consisting of saturated calomel electrode as reference electrode, platinum mesh as a counter electrode, and sol–gel prepared MnO_2 mounted on Ti mesh used as working electrode. Aqueous NaCl, KCl, Na_2SO_4 and LiCl solutions were used as electrolytes. The ambigel form of MnO_2 showed high capacitance compared to that of the xerogel form of MnO_2. Maximum capacitance of 130 F/g was obtained at a scan rate of 5 mV/s for the ambigel form of MnO_2 in a 2M NaCl solution. Effect of NaCl concentration on the capacitance of MnO_2 was studied. Stability of MnO_2 was studied up to 800 cycles. [14]

B) A layered δ-MnO2 nanoflake cathode with high zinc-storage capacities for eco-friendly battery applications

This study reports the use of a layered-type birnessite δ-MnO2 nano-flake cathode for eco-friendly zinc-ion battery (ZIB) applications. The present δ-MnO_2 was prepared via the simple low temperature thermal decomposition of $KMnO_4$. The X-ray diffraction (XRD) pattern of the samples was well indexed to the δ-MnO_2 phase. Field emission SEM and TEM images of the δ-MnO_2 revealed flake-like morphologies with an average diameter of 200 nm. The electrochemical properties, investigated by cyclic voltammetry and constant current charge discharge measurements, revealed that the nano-flake cathode exhibited first discharge capacity of 122 mAh g^{-1} under a high current density of 83 mA g^{-1} versus zinc. The discharge capacity thereafter increased until it reached 252 mAh g^{-1} in the fourth cycle. On the hundredth cycle, the electrode registered a discharge capacity of 112 mAh g^{-1}. Coulombic efficiencies of nearly 100% were maintained on prolonged cycling and thereby indicate the long cycle stability of the δ-MnO_2. Besides, the realization of specific capacities of 92 and 30 mAh/g at high current densities of 666 and 1333 mA/g, respectively, clearly demonstrates the decent rate capabilities of δ -MnO_2 nano-flake cathode. These results may facilitate the utilization of layered-type birnessite δ-MnO_2 in ZIB applications. [15]

C) Bi-electrocatalytic property of MnO_2 nanoparticles modified electrodes to H_2O_2

An interesting mode of reactivity of MnO_2 nanoparticles modified electrode in the presence of H_2O_2 is reported. The MnO_2 nanoparticles modified electrodes show a bi-direction electrocatalytic ability toward the reduction/oxidation of H_2O_2. Based on this property, a choline biosensor was fabricated via a direct and facile electrochemical deposition of a biocomposite that was made of chitosan hydrogel, choline oxidase (ChOx) and MnO_2

nanoparticles onto a glassy carbon (GC) electrode. The biocomposite is homogeneous and easily prepared and provides a shelter for the enzyme to retain its bioactivity. The results of square wave voltammetry showed that the electrocatalytic reduction currents increased linearly with the increase of choline chloride concentration in the range of $1.0x10^{-5}$ – $2.1x10^{-3}$ M and no obvious interference from ascorbic acid and uric acid was observed. Good reproducibility and stability were obtained. [16]

D) Interfacial synthesis of porous MnO_2 and its application in electrochemical capacitor

The porous manganese dioxide (MnO_2) was prepared by an interfacial reaction of potassium permanganate in water/ferrocene in chloroform. The surface area and pore distribution of MnO_2 can be controlled by simply adjusting the reaction time and the content of surfactant in the aqueous phase. The electrochemical performance of the prepared MnO_2 was evaluated as an electrode material for supercapacitors by the means of cyclic voltammetry and Galvano static charge–discharge tests. Electrochemical tests results indicated that the pore size plays an important role at high charge–discharge rate, the sample with a large pore size shows a better rate capability, while the sample with a small pore size but large surface area delivers a large capacitance at low current rate. [17]

E) Plasma-Assisted Growth of β-MnO_2 Nanosystems as Gas Sensors for Safety and Food Industry Applications

The development of efficient sensors for security field and food quality control applications has gained an ever-increasing attention for various end-uses. In this context, this work reports on the preparation of β-MnO_2 nanosystems by plasma enhanced-chemical vapour deposition (PE-CVD), using a fluorinated Mn(II) diamine-diketonate as single-source precursor for both Mn and F. Modulations of oxygen partial pressure enable to tailor not only the morphology and oxygen vacancy content, but also fluorine doping level of the resulting systems. For the first time, the gas sensing performances of PE-CVD β-MnO_2 nanomaterials are tested in the detection of acetonitrile, a poisonous chemical warfare agent (CWA) simulant, and ethylene, an important marker of fruit ripening. The obtained results demonstrate that the fabricated sensors can efficiently detect these analytes, with the best responses at moderate temperature (≤200 °C), enhanced by a higher oxygen vacancy content and fluorine concentration. These features, coupled with the good selectivity and response times, candidate the developed systems as amenable platforms for practical applications. [18]

CONCLUSION

MnO_2 is an electrochemically active substance and thus used for various electrochemical processes. It has a wide range of applications in various technological advancements that are present in today's date. All polymorphs of MnO_2 have different characteristics that are useful to us in many ways. Electrochemical studies of these polymorphs give a lot of information about their uses and gives us various more applicative properties that can be used potentially well.

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