

NANOSTRUCTURED MANGANESE OXIDE FROM GHANA'S MANGANESE ORE FOR LITHIUM-ION BATTERY ANODE

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Abstract

The manganese ore deposit, which is one of the precious minerals mined in Ghana is valued at 42.5 million tons in 2014. The development of this mineral in Ghana is reduced to mining, crushing, categorization, and finally export. This brings little foreign exchange to the country since the oxide or carbonate of manganese in its natural state is of relatively little commercial importance. Treating and converting this manganese deposit into metal or other more valuable manganese-based products will improve the commercial value and subsequently enhance Ghana's economy via job creation and foreign exchange. In this study, we synthesized nanostructured manganese oxide from naturally occurring Ghanaian manganese oxide-containing ore through a mild acid leaching process. The Field Emission Scanning Electron Microscope (FESEM) image showed well-developed porous structures on the surface of the synthesized nanostructured manganese oxide particles. The electrochemical properties of the synthesized manganese oxide used in lithium-ion battery demonstrated an initial discharge capacity of 1550 mAh/g and retained about 76% of the discharged capacity after the 5th discharge cycle from the 2nd discharge cycle. The cycle performance showed better stability after the 13th cycle and after the 27th cycle, the cell retained about 38% of the discharged capacity from the 2nd discharge cycle. From the above results, it can be concluded that synthesized nanostructured manganese oxide from Ghana's manganese ore stands the chance of being utilized as anode material in lithium-ion batteries but further studies and modification would be needed to enhance its performance.

Keywords

MnO₂; Nanostructure; anode material; Lithium ion battery; cyclic voltammetry; Charge-discharge

Introduction

Manganese (Mn) is a common ferrous metal that constitutes roughly 0.1 percent of the earth's crust; making it the 12th most abundant element. Mn is one of the most abundant metals in soils, where it exists as oxides and carbonate. Mn occurs mainly as pyrolusite (MnO₂), and to a lesser extent as rhodochrosite (MnCO₃) (Önal et al., 2021). The top six (6) mining countries for Mn ores in 2020 are China, South Africa, Australia, Gabon, Ukraine, and Ghana respectively (Garside, 2021). In 2020, an estimated 1.4 million metric tons of Mn was produced in Ghana. This stood against the over 4.5 million metric tons produced in 2018, which was the highest since 2009 (Sasu, 2021). The Nsuta Ghana Mn ore is high-grade ore, which is considered to have one of the highest manganese-to-iron ratio ores in the market (Mn: Fe~3:1). Low in phosphorous, alumina, and other heavy metal impuri-

ties, making it well-suited for both alloy and manganese metal production (GMC, 2021). In 2018, the Ministry of Finance recorded export of 4.4 million metric tons of Mn to other countries (MoF, 2019). The development of Mn ore in Ghana is reduced to mining, crushing, categorization, and finally export. This brings little foreign exchange to the country since the carbonate of Mn in its natural state is of little commercial importance. Treating and converting this Mn deposit into the metal form or other more valuable manganese-based products will bring more economic benefit to Ghana.

Over the years researchers have tried adding value to the Mn mined in Ghana. In 1996, Momade reported the investigation of sulphuric acid leaching of manganese ore from Nsuta. He studied the concentration of Mn in the ore and other parameters that enable the effective extraction of the Mn ions from the ore (Momade, 1996). Again in Ali and Amankwah

(2013) reported the enrichment of manganese oxide tailings generated by spiral concentration plants at the Ghana Manganese company. They obtained the highest grade of Mn which qualifies as medium-grade material in the Mn market (Ali and Amankwah, 2013). Recently Amankwah and Pickles (2005) demonstrated the application of microwave energy in the pretreatment step in the calcination and sintering of the Ghana Mn ore. Nimako et al. (2020) demonstrated the calcination behaviour of Nsuta manganese ore in the presence and absence of end-of-life high-density polyethylene to establish a fundamental understanding of the calcination behaviour of the Nsuta manganese ore using waste plastics.

Over the years, little has been done in producing manganese-based products and their useful practical application in Ghana. In Egypt, Shaaban et al. (2017) worked on developing reliable processes for the production of some selected manganese compounds using Mn ores from Sinai. Zhao et al. (2013) investigated the preparation of chemical manganese dioxide from low-grade rhodochrosite ore from China for use in the chemical industry. Malankar et al. (2010) reported the characterization of γ - MnO_2 obtained from manganese ore from Kanhan mines, Nagpur, India, as cathode vs Zn anode in alkaline Zn- MnO_2 battery. In Brazil, Mendes et al. (2019) also proposed a low-cost starting material for the preparation of lithium manganese oxide from manganese mining residue for lithium-ion battery (LIB) application. The lithium-ion battery has attracted a lot of attention among secondary batteries due to their promising usage in electric vehicles and power grids as a clean energy source (Goodenough and Park, 2013; Mohanty et al., 2014). The past decade has seen the shifting in the application of the LIB from common consumer electronics to sophisticated applications including the locomotive industry. In the automobile industry today, LIB has been used as an electrification system for vehicles including hybrid vehicles, plug-in hybrid electric vehicles, and fully electric vehicles (Office of energy efficiency and renewable energy, n.d, 2012; Zhou and Stephens, 2014).

This preliminary work is aimed to produce nano-structured MnO_2 through an acidic solution leaching from a local manganese ore from Ghana and ascertain its potential application as an anode material for lithium-ion batteries. MnO_2 has drawn much attention as an anode material. The several crystal structures and many valence states of manganese ions can facilitate multiple electron transfer and achieve higher theoretical capacity (1230 mAh/g) (Park et al., 2020). Among the various chemical processes such as hydrothermal (Darr et al., 2017), sol-gel process Parashar et al. (2020), microemulsion Soleimani Zohr Shiri et al. (2019) for the synthesis of nanoparticles, the traditional co-precipitation methods are widely accepted commercially because it is cost-effective, simple, and produce rapid results (Julien et al., 2016; LaGrow et al., 2019). This process enables the control of particle size and composition, the modification of particle surface, and homogeneity. Topically, advancements in nanotechnology have stimulated the production of nanostructured materials

(particles with size ≈ 100 nm or less) which have a rich mixture of tenable physical properties which are different from their macro-sized counterparts because of their morphology, polymorphism, particle sizes, particle-size distribution, and the precursors utilized in the preparation (Zhan et al., 2018; Zhang et al., 2020).

Materials and Methods

Materials

The manganese mineral was acquired from the earth science Department at the University of Ghana (initially got from the Nsuta Wassa deposit site in the Wassa West District of the Western Region of Ghana). Ammonium carbonate (NH_4CO_3 , 99%), and Sulfuric acid (H_2SO_4 , 98%) were bought from Sigma Aldrich and utilized without any additional preparation. A standard commercial liquid electrolyte (PanaX Etec) consisting of 1.2 M LiPF_6 dissolved in EC/DMC = 1:3 volume ratio was purchased from Sigma-Aldrich and was dried in a vacuum chamber for at least 12 hours.

Methods

Synthesis of MnO_2 from Manganese ore

The leaching of the manganese oxide into solution from the manganese rock specimen follows the technique reported by Li et al. (2015); Momade and Momade (1999). The primary elemental composition of the mineral rock specimen was obtained through x-ray fluorescence (XRF) spectroscopy. In a representative synthesis methodology, the manganese-containing rock sample was crushed, ground, and afterward sieved to the necessary particle size, utilizing a 300 μm mesh-sized sieve. Approximately 10 g of the sieved manganese-containing powder specimen was added to a beaker containing 100 ml (1.8 M) dilute H_2SO_4 solution. The mixture was then placed on a hot plate/magnetic stirrer, mixed for 2 hours at a temperature of 60 $^\circ\text{C}$; after which it was cooled, the mash filtered. About 15–24 g of NH_4CO_3 was added step by step to the filtrate under consistent stirring to precipitate out MnCO_3 . The as-formed MnCO_3 particles were washed a few times with distilled water-ethanol solution and afterward oven dried at 80 $^\circ\text{C}$ overnight. The dried MnCO_3 powder was calcined in ambient atmosphere utilizing an electric muffle furnace at 400 $^\circ\text{C}$ for 2 hours to convert it into MnO_2 particles (Jiang et al., 2016). The final product was characterized utilizing X-Ray Diffraction, Scanning Electron Microscopy, Thermogravimetry, Fourier Transform Infrared spectroscopy, chemisorption, and electrochemistry.

Characterization of MnO_2 ore and the synthesized MnO_2 particles

Elemental composition of the raw manganese oxide mineral rock specimen was carried out on a Thermo Fisher ARL9400 XP+Sequential X-Ray Fluorescence machine outfitted with WinXRF software for investigations. Before the investigation, the specimen was pulverized in a tungsten-carbide processing media to attain particle sizes of <75 μm . A PVA binder

was blended in with it and pressed into a pellet utilizing a 10-ton hydraulic powered press. To examine the different phases present, as well as the microstructure of the prepared MnO₂ nanoparticles, X-ray powder diffraction (XRD) data was taken on a Rigaku ultra-X diffractometer (Rigaku Co., Japan) which has a Bragg-Brentano geometry and working with a Cu K α radiation x-ray tube ($\lambda = 1.5418$ Å) at 40 kV and 120 mA. The XRD profile of the powder specimen was recorded in the 10°–90° 2 θ range with a step size of 0.017°, the step scan rate of 0.02°, and a counting time of 14 s per step. The diffraction profile was then matched against the ICSD's PDF database and qualitative phase analysis done by means of the X'Pert Highscore plus search match software (Panalytical, Netherlands).

A high resolution SU5000 (HITACHI, Japan) field emission scanning electron magnifying microscope (FESEM) operating at 2.0 kV was utilized in the surface morphological examination of all the samples in this study. Before the SEM investigation, the specimens were coated with carbon covering to make them conductive and permit higher amplifications. The groups of atoms responsible for the characteristic behavior of the various class of compounds on the surface of the MnO₂ particles were recorded on a Bomem MB100 (ABB Bomem, Canada) Fourier Transform Infrared (FTIR) spectrometer. Spectra information were recorded within the 4000 - 600 cm⁻¹ spectral range in transmission mode and analysed utilizing the GRAMS/AI™ Spectroscopy Software Suite. Thermal examination was conducted utilizing a Thermtest TGA-n 1000 thermal analyzer (Thermtest Instruments, USA) outfitted with the Infinity Pro Thermal Analysis software. About 3.45 mg of the specimen was put in an alumina (Al₂O₃) crucible (50 mg limit), subjected to a linear heating ramp between 20 °C and 1000 °C at a rate of 10 °C/min and a cooling rate of 50 °C/min in a nitrogen atmosphere. The measurements were made for the mass change (loss/gain) of the specimen as a function of temperature. Specific surface area and porosity estimations were done on a Micromeritics TriStar II 3020 sorption analyzer utilizing the multipoint Brunauer-Emmett-Teller (BET) standard approach. Before the estimations, the specimen (~0.1394 g) was degassed under vacuum at 300 °C for 24 hours in a nitrogen atmosphere and an adsorbate at 77.3 K. Full isotherm data was recorded within relative pressures of 4E⁻⁶ to 1.

Preparation MnO₂ anode and electrochemical analysis

The MnO₂ anode consisting of a slurry including 80 wt.% as-prepared MnO₂ active material, 10 wt.% Carbon-black Super-P (Timical super PTM) as conducting agent, and 10 wt.% polyvinylidene fluoride (PVDF, Kreha, Japan, Mw = 350,000) as the polymeric binder in N-methyl-2-pyrrolidone (NMP, Sigma Aldrich) as a dispersing agent. The viscous slurry was cast on a copper foil (30 µm, Iljin Materials, Korea) via doctor blade apparatus. The coated slurry was dried at 120 °C for 2 hours and then pressed with a roll pressing machine (WV-60, Samyang 60, South Korea). The electrode coat obtained was about 35–50 µm and the average loading mass was 1.2–2.2

mg/cm². The surface morphology of the as-prepared electrode was investigated utilizing a field-emission scanning electron microscope (Hitachi S-4800).

Coin cell assembly and electrochemical property

The half cells assembled in a coin type cell CR2032 and in an argon-filled glove box consisted of lithium metal (14 mm, 99.99% Aldrich) as counter and reference electrode, and the fabricated MnO₂ electrode as the working electrode. 1.2 M LiPF₆ (EC/DMC = 1:3 volume ratio, Panax Etec, Korea) and polyethylene separator (PE, 18 mm, 20 µm, celgard) were used as the electrolyte and separator respectively. Cyclic voltammograms (CVs) of the MnO₂ discharging-charging cycles were measured at a scan rate of 0.05 mV/s in the potential range of 0.01 ~ 3.0 V using Autolab (ECO CHEMIE PGSTAT 100). The formation step was performed by discharging and charging at room temperature in the same potential range, discharging and charging the cell from 0.05 to 3.0 V (versus Li/Li⁺) at a constant current of 100 mA/g using charge/discharge cyler (PNE Solution, Korea). All the cells were kept for 12 hours before electrochemical measurement. Electrochemical impedance spectroscopy was used to measure the total resistance of the cells in a frequency range of 10⁻² – 10⁶ Hz at open circuit potential (OCP).

Results and Discussion

Elemental composition of Manganese Ore and X-Ray Diffraction Analysis (XRD)

The elemental constituents as well as the physical and chemical properties of any material have a critical influence on its technological applications. From the XRF examination, it was observed that the manganese rock specimen comprised a high level of manganese and other minor components as follows: Mn (78.00%); Al (9.52%), Si (8.22%), Fe (1.83%), K (0.63%), Ni (0.39%), Zn (0.23%), Ca (0.22%), P (0.14%), and others (0.83%).

The XRD profile (Figure 1a) shows transcendently MnO₂ nanoparticles with both alpha and gamma phases. The profile shows peaks with wide base and narrow tips; proposing the presence of a multimodal crystallite size distribution in the prepared powder. Quantitative microstructural data were acquired from the XRD information utilizing the whole Powder Pattern Modelling (WPPM) approach (Scardi and Leoni, 2002), which straightforwardly interfaces an actual model for the microstructure with the diffraction profile, allowing a pulling out of microstructure parameters without resorting to arbitrary peak shapes in order to fit each diffraction peak. This is a more exact methodology contrasted with the traditional Line Profile Analysis dependent on the Williamson-Hall or Warren-Averbach techniques (Scherrer, 1918; Warren, 1990). Figure 1b shows the diffraction pattern of the MnO₂ particles modelled by means of the WPPM. The modelling was conducted by assuming the presence of a lognormal distribution of multimodal sized spherical domains; and to take care of the possible surface relaxation effects usually seen in nanocryst-

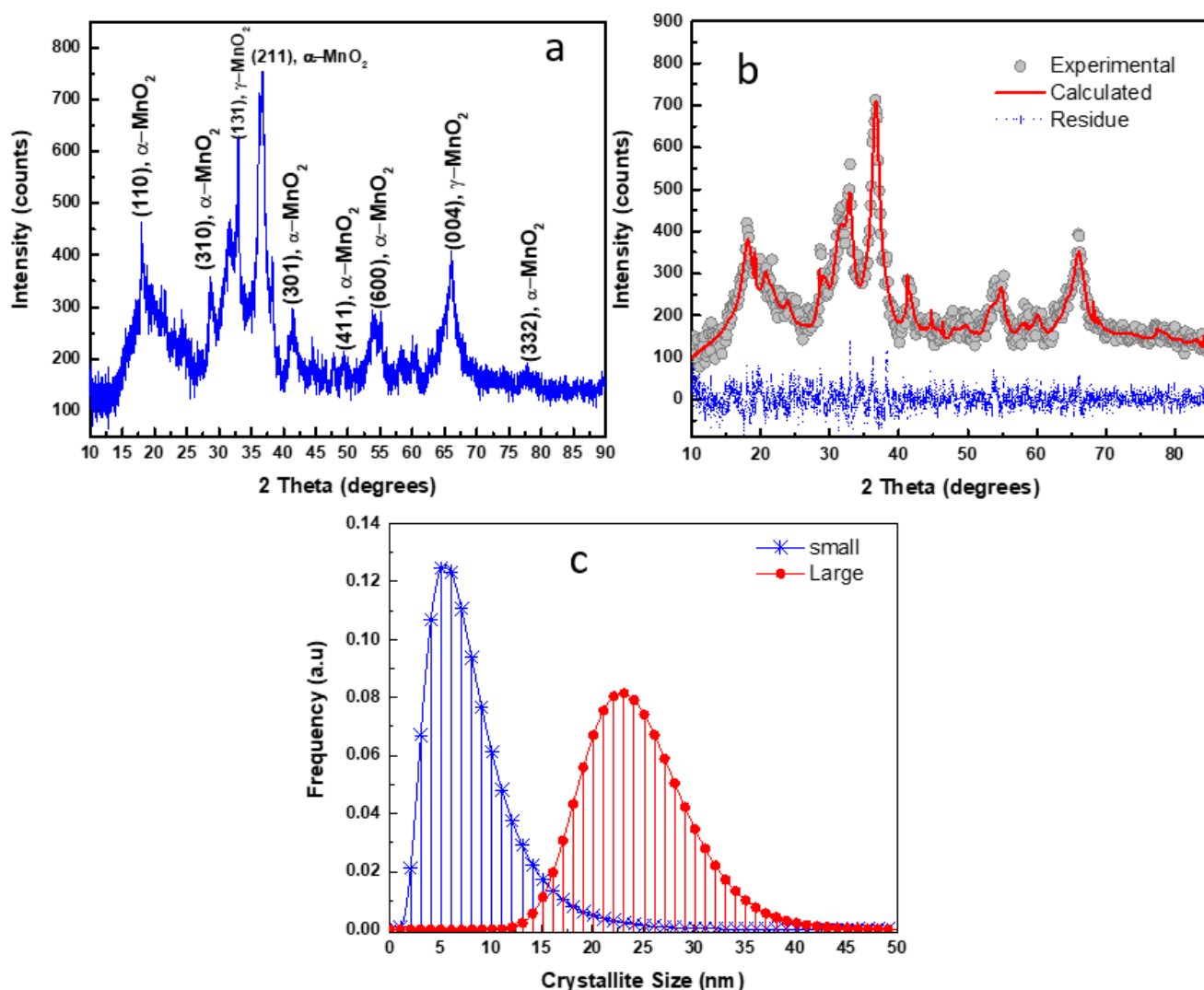


Figure 1. (a) X-ray diffraction pattern, (b) WPPM result: experimental data (circle), calculated data (line) and difference between the two (residual, line below) and, (c) Lognormal distribution of the small and large crystals of the as-synthesized MnO₂ nanocrystals specimen.

talline powders (M and P, 2004; Nunes and Lin, 1995). The residual (the contrast between the modelled and experimental information) was not totally level and unexceptional, as it would be foreseen in the occasion of a decent match. This observation in the modelling could be ascribed to the non-ideal states of the XRD measurements and perhaps, a more intricate size distribution. From the lognormal distribution of spheres (Figure 1c), the nominal crystallite size ranges from ~ 8 nm (little) and 26 nm (huge).

Scanning Electron Microscopy analysis

The pulverized manganese-containing powder (Figure 2a) had a wide distribution of particles because of the grinding process. After the leaching process, the as-acquired MnO₂ nanoparticles (Figure 2b) show a lot finer particles with some agglomerations and a much smaller dispersion of particle sizes which is predictable with the perception from the XRD and

BET viewpoints. The electrode material (Figure 2c) shows very much spherical porous particles which are all well connected by the binder and great bond on the current collector substrate: a significant feature for good charge transport.

FTIR spectroscopy and Thermal stability

Figure 3a displays FT-IR spectrum of the MnO₂ nanoparticles. The exceptionally weak bands around 4000–3500 cm⁻¹ and 1637.96 cm⁻¹ relate to the O–H vibrational mode of adsorbed water. Additionally, the two low peaks around 2338 cm⁻¹ and 2361 cm⁻¹ can be attributed to the stretching vibrations modes of CO₂ (Barichard et al., 2008; Fermo et al., 2006), which was brought about by the absorption of atmospheric carbon dioxide during the heat treatment cycle. The absorption bands at 1388.96 cm⁻¹, relates to the O–H bending vibrations attached together with the Mn particles; while the absorption band at 2081 cm⁻¹ emerged because of the unique

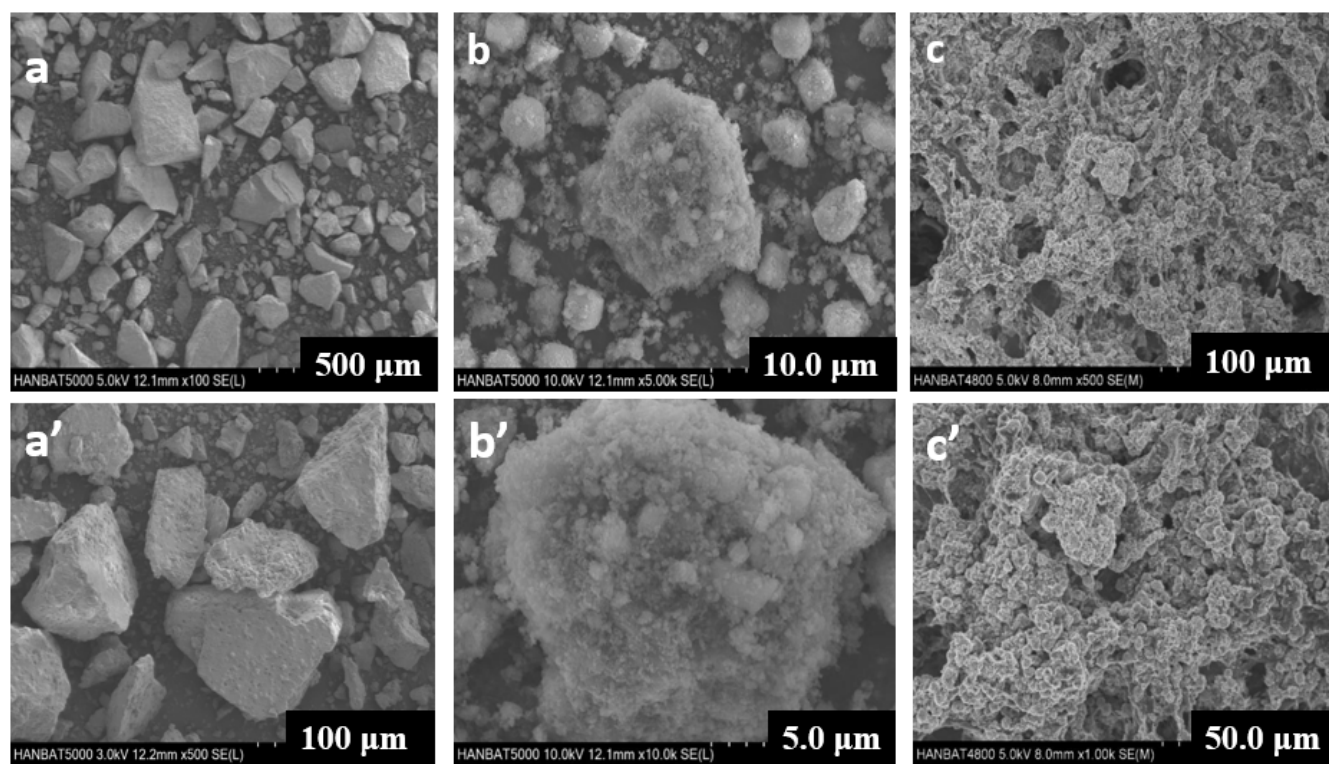


Figure 2. SEM Micrographs at different magnifications for (a, a') manganese ore, (b, b') as-prepared MnO₂ nanoparticles and (c, c') MnO₂ electroactive electrode

level of hydrogen bonding inside the sample. The presence of O–H vibrations in the FTIR spectrum indicates the presence of adsorbed molecular water within the MnO₂ structure. This hydrating property of the MnO₂ could improve the cation diffusion process and hence an increment in the capacitance of MnO₂ nanoparticles. The absorption peaks under 1320 cm⁻¹ can be ascribed to the surface –OH groups of Mn–OH of MnO₂ nanoparticles (Jaganyi et al., 2013).

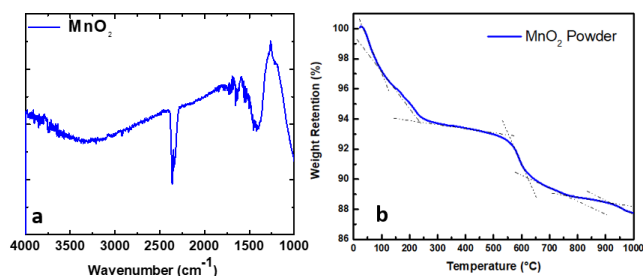


Figure 3. (a) FTIR of the MnO₂ nanoparticles (b) Thermogravimetric stability of the MnO₂ nanoparticles

The thermal stability of the as-synthesized MnO₂ nanoparticles was completed in the range of 20 °C and 1000 °C by The thermal stability of the as-synthesized MnO₂ nanoparticles was completed in the range of 20 °C and 1000 °C by Thermogravimetric Analysis (TGA) as shown in Figure 3b. The variations of the TGA thermogram of MnO₂ nanoparticles are introduced in the temperature range of 22–132 °C, 132–236 °C; 236–557 °C, 663–777 °C, 768–920 °C, 920–1000 °C.

The primary weight reduction occurring between ~22–132 °C is related to the dehydration of the MnO₂ nanoparticles. The second weight reduction in the range of 132–236 °C and 236–557 °C could be identified with the evaporation of the surface adsorbed water molecule or intercalated in the MnO₂ nanoparticles crystal structure potentially prompting the phase transition of layered to tunnelled MnO₂. The subsequent weight loss in the sample occurs between 557 °C - 1000 °C as seen in the TGA thermogram (Figure 3b), could be identified with the expulsion of oxygen from manganese oxide cross section, attributable to the stage change of MnO₂ to Mn₂O₃ and the end of intercalated anions for example chloride particles. The TGA diagram displayed an all-out weight reduction of 12.3% during the whole heating period.

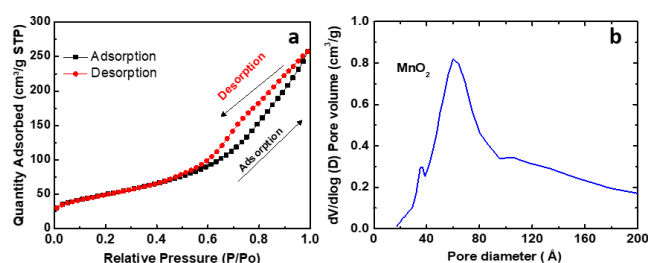
BET Surface area and Barrett-Joyner-Halenda (BJH) Porosimetry Analysis.

The surface area and the pore features of the as-produced MnO₂ was investigated by assessing the N₂ adsorption–desorption isotherms. The nitrogen adsorption-desorption isotherm of the MnO₂ nanoparticles shown in Figure 4a is of the normal type IV design with distinctive H2 and H3 hysteric loop in within 0.4–0.8 P/P0 and 0.9–1.0 P/P0, respectively; demonstrating the presence of microporous and mesoporous structures as indicated by the IUPAC classification (Sing, 1985). These bimodal pore structures and distribution are beneficial to the improvement of oxidation efficiency because of the quicker diffusion of different reactants and by-products (Chen

Table 1. BET pore structures and surface areas of the synthesized MnO₂ nanoparticles compared to other analogous works.

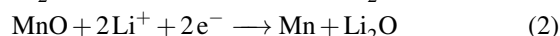
Sample	BET surface (m ² /g)	Average pore diameter (nm)	Total pore volume (cm ³ /g)	Reference
Nanoparticles α -MnO ₂	135.0	6.02	0.210	(Zhang et al., 2012)
Flower-like α -MnO ₂	69.5	11.70	0.240	(Zhang et al., 2012)
Nanorods α -MnO ₂	22.5	12.17	0.072	(Zhang et al., 2012)
Nanostructured α -MnO ₂	126.7	15.2	-	(Jang et al., 2016)
Nanoparticles α -MnO ₂	57.449	6.95	0.245	(Sahib and Naser, 2021)
Nanostructured α -MnO ₂	178.42	7.42	0.398	This work

and Dionysiou, 2008). The equivalent information on the distribution of pore sizes of the MnO₂ nanoparticles (see Figure 4b) was determined through the Barrett-Joyner-Halenda (BJH) procedure from the adsorption part of the isotherm. The analysis brought about the BET surface area of 178.42 m²/g, BJH surface area of 215.12 m²/g, total pore volume of 0.398032 cm³/g and average pore size of 7.42 nm. Table 1 shows the data regarding the BET surface areas, average pore sizes, and total pore volumes of the synthesized MnO₂ nanoparticle compared with similar works.

**Figure 4.** (a) Adsorption-Desorption isotherm of the as-obtained MnO₂ nanoparticles (b) pore size distribution of the as-obtained MnO₂ nanoparticles

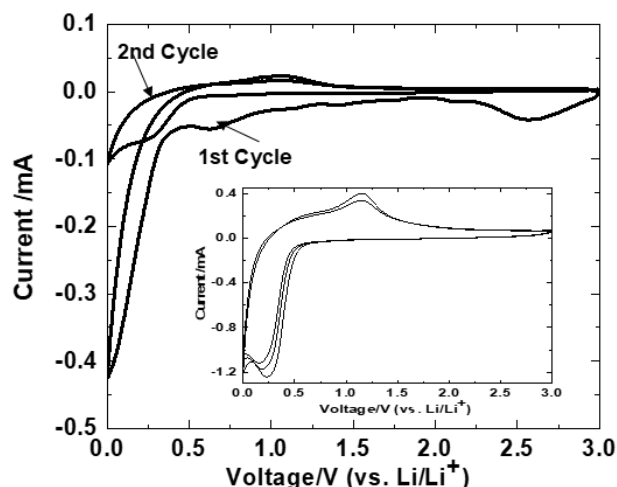
Electrochemical properties of the obtained MnO₂ anode

Figure 5 shows the CV profile of the first two cycles of the cell containing the nanostructure anode. The cell was tested in the potential range of 0.01–3 V at a scan rate of 0.05 mV/s. Scanning in the negative direction, a wide reduction peak is observed at around 2.6 V, and smaller peaks at around 2.25 V and 1.5 V corresponding to the electrolyte decomposition and the formation of the solid electrolyte interface (Lai et al., 2012; Li et al., 2014). The cathodic peak reduced drastically after the first cycle showing that the formation of the Solid electrolyte interface (SEI) layers is dominant in the first cycle (Li et al., 2013, 2012). The cathodic peak located around 0.7 V matches the reduction of MnO₂ to MnO (see equation 1) and the subsequent reduction of MnO to Mn (see equation 2).



In the second cycle of the CV curve, the cathodic peak located at 0.7 V shifted further in the negative direction at 0.25 V due to the formation of Li₂O and the metallic manganese (Chen

et al., 2014). Scanning in the positive direction, a broad anodic peak is observed at a potential of 1.1 V conforming to the reversible phase change from MnO₂ to Mn and from Mn to MnO₂ during the intercalation and deintercalation of lithium in the nanostructured MnO₂ (Liu et al., 2016). Additionally, good structural stability and excellent electrochemical reversibility is observed in the subsequent cycles following the overlap of the anodic and the cathodic curves (see the insert in Figure 5). The electrochemical charge-discharge performance

**Figure 5.** CV of the MnO₂ anode measured at a scan rate of 0.05 mV/s in the potential range of 0.01~3.0 V.

of the anode electrode based on the synthesized nanostructured MnO₂ was investigated. Figure 6 shows the first five charge-discharge curve of the half-cell consisting of lithium metal as the reference electrode. From the charge-discharge curve, the cell delivered an initial discharge capacity of 1550 mAh/g which is higher than the theoretical discharge capacity of MnO₂ (~1230 mAh/g) (Li et al., 2013). This extra capacity may be attributed to the irreversible formation of the SEI layer. In the first discharge curve, three plateaus can be observe. One long one at a potential of 0.5–0.25 V corresponding to the reversible reduction of MnO₂ (Jiang et al., 2016) and two short ones at 1.5 V and 1.8 V matching the formation of the SEI layer on top of the synthesized nanostructure MnO₂ (Julien et al., 2004; Zhang et al., 2016). In the first charge curve, a long plateau is observed around 1.15 V corresponding to the oxidation of Mn to MnO₂ during the de-intercalation of lithium comparable to the anode peak in the CV curves (Li

et al., 2013). Furthermore, a reversible and stable electrochemical process is observed after the first charge-discharge cycle as witnessed in the subsequent charge-discharge curves.

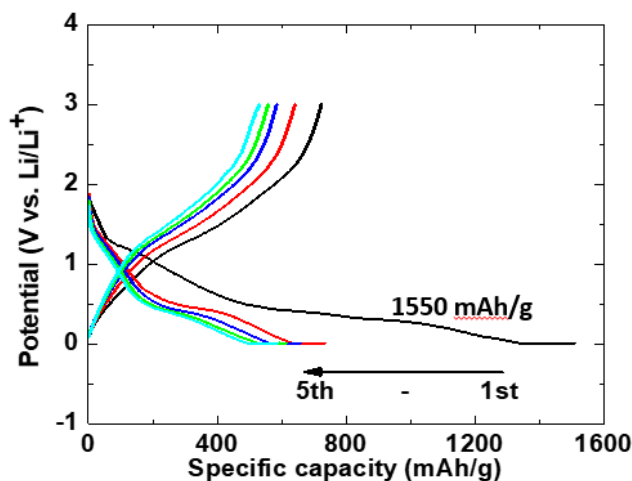


Figure 6. Charge-discharge curves of MnO₂ anode materials in the potential range of 0.01~3.0 V and a current density of at 100 mA/g.

The cycling performance of the as synthesized nanostructured anode at a potential range of 0.01–3.0 V and a current density of 100 mA/g is depicted in Figure 7. An extreme capacity fading is observed within the first charge-discharge cycle which may be attributed to the SEI layer formation on the surface of nanostructure MnO₂ anode from the decomposition of electrolyte solvent. Table 2 shows the electrochemical properties of different MnO₂ anode electrode for lithium-ion battery. The MnO₂ synthesised from the Mn-Ore showed promising electrochemical performance in comparison to other reported in other studies. Subsequently, with increasing cycle number, the capacity of the nanostructured MnO₂ anode fades gradually. However, after 27 cycles, the nanostructured MnO₂ anode retained about 619 mAh/g of lithium-ion storage capacity signifying a 38% decrease in storage capacity. The general performance of the synthesized nanoparticles is facilitated by the high surface area of the nanostructures and the available short ionic diffusion length in the electrodes. Data from the XRD confirms that the synthesized nanoparticles is a composition of hollandite (α -MnO₂) and nsutite (γ -MnO₂) with tetragonal and complex tunnel respectively (Julien et al., 2004). Again from the XRD and the FESEM data, it can be concluded that the particles are more amorphous in nature (less crystalline) and therefore the high specific capacity obtained for the synthesized particles. The intergrowth of diverse tunnels structure throughout the particles are responsible for the easy movement of lithium ions (Brousse et al., 2006). The resistive behavior of the fabricated nanostructured anode was investigated using electrochemical impedance spectroscopy. The Nyquist plot measured in the frequency range of 10^{-2} – 10^6 Hz is shown in Figure 8. From the plot, it can be observed from the plot intercept the real-axis (Z') at a point. This point

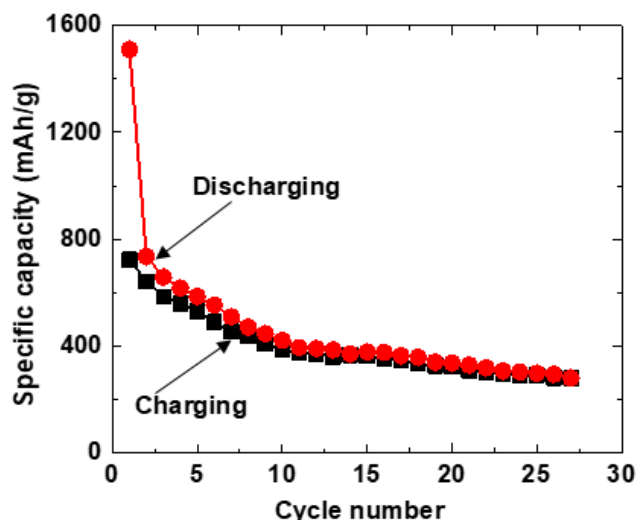


Figure 7. Cycling performance of the nanostructured MnO₂ anode in the potential range of 0.01~3.0 V and a current density of at 100 mA/g.

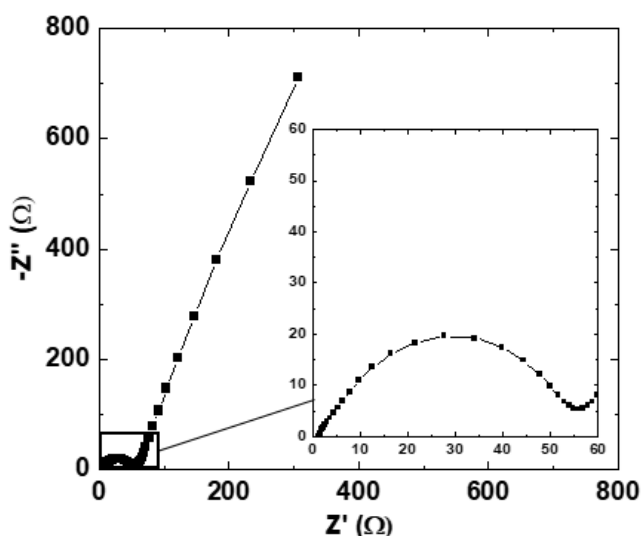


Figure 8. The Nyquist plot (CIS) for the synthesized MnO₂ nanoparticles

represents the overall resistance in the solution, including the electrode material, diffusion of the ions in the electrolyte and the resistance between the active material and the current collector (Gamby et al., 2001; Ye et al., 2005). The plot is also characterized by a semicircle in the middle frequency region and a straight line included at 45° in the low-frequency region. The semi-circle corresponds to the charge transfer resistance and the straight line in the low-frequency region is the lithium-ion diffusion in the MnO₂ nanostructure electrode. From the insert in Figure 8, it can be observed that the cell with the nanostructured MnO₂ anode experiences less solution resistance and interface contact and therefore less charge transfer resistance. This property is favourable for enhancing the electrochemical performance of the MnO₂ anode.

Table 2. Summary of electrochemical performance of the as-prepared MnO₂ material in comparison to published work

Electrode	Method of preparation	Electrolyte	Cell type	Voltage (V vs. Li/Li ⁺)	Current Density (C-rate)	2nd Specific Capacity (mAh g ⁻¹)	5th Specific Capacity (mAh g ⁻¹)	Reference
Caddice-clew-like MnO ₂	Hydrothermal from MnSO ₄ ·H ₂ O	1 M LiPF ₆ (1:1, EC:DMC)	half-cell	0.01–3.60	0.2	500	356	(Feng et al., 2014)
urchin-like MnO ₂	Hydrothermal from MnSO ₄ ·H ₂ O	1 M LiPF ₆ (1:1, EC:DMC)	half-cell	0.01–3.60	0.2	600	465	(Feng et al., 2014)
MnO ₂ nanorods	Hydrothermal from KMnO ₄	1 M LiPF ₆ (1:1:1, EC:DMC:DEC)	half-cell	0.01–3.0	0.1	1,326	-	(Chen et al., 2014)
3D δ-MnO ₂	Chemical synthesis using Mn(NO ₃) ₂ ·H ₂ O	1 M LiPF ₆ (1:1:1, EC:DMC:EMC)	half-cell	0.01–3.0	0.1	905	-	(Voskanyan et al., 2019)
δ-MnO ₂	Hydrothermal from MnSO ₄ ·H ₂ O and KMnO ₄	1 M LiPF ₆ (1:1:1, EC:DMC:EMC)	half-cell	0.01–3.5	0.1	1060	802	(Zhan et al., 2018)
Nanostructure -MnO ₂	Chemical synthesis from Mn-Ore	1 M LiPF ₆ (1:3, EC/DMC)	half-cell	0.01–3.0	0.1	776	690	This work

NB: EC - ethylene carbonate, DMC - dimethyl carbonate, DEC - diethylene carbonate, LiPF₆ - Lithium hexafluorophosphate, KMnO₄ - Potassium permanganate, MnSO₄·H₂O - Manganese (II) sulfate hydrate Mn(NO₃)₂·H₂O - Manganese (II) nitrate hydrate

Conclusion

Nanoparticles of MnO₂ were successfully produced through an acidic solution leaching strategy from a local high-grade manganese-containing rock specimen from Ghana. The calcination of the leached intermediate MnCO₃ powder at 400 °C for 2 hours brought about fine MnO₂ nanoparticles (8–26 nm) with a crystallographic structure of blended α and γ phases and bimodal crystallite size distribution as affirmed by x-ray diffraction and microscopy techniques. The prepared cell with the prepared nanostructured MnO₂ anode offered a high initial discharge capacity of 1550 mAh/g and a fairly excellent cycling performance. The morphological structure of the as-prepared nanostructured MnO₂ assisted in the movement and diffusion of ions in the electrolyte easily. The after-effects of the electrochemical assessments recommend that the as-prepared MnO₂ nanoparticles have the potential for use as anode materials for LIB. However, further studies and modifications such as combining MnO₂ with other materials (example carbon) to thwart volume expansion or improve cycle performance are required.

Recommendation

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