

MANGANESE OXIDE BASED CORE@SHELL NANOPARTICLES AND ITS APPLICATION IN AQUEOUS ZINC-ION BATTERY

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ABSTRACT

In this study, MnO₂ as well as core@shell type MnO₂@Ag material were prepared through the versatile reverse micelle route. FTIR absorption band at 522 cm⁻¹ was ascribed to the Mn-O stretching mode, demonstrating the presence of a Mn-O bond inside the MnO₂ structure. XRD was used to determine the crystalline structure of the prepared samples. Peaks at 2θ = 12.7°, 18.1°, 28.8°, 37.5°, 42.1°, 49.9°, 56.2°, and 60.3° matched the α-MnO₂ diffraction peaks nicely. The spherical shape of the produced MnO₂ and MnO₂@Ag compounds was observed in FESEM. The results of the histogram show that MnO₂@Ag particles are marginally smaller than MnO₂ particles. The electrochemical assessment of the generated cathode materials for aqueous zinc-ion battery (AZIB) CR-2032 was conducted using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and battery charge-discharge (BCD) techniques.

Keywords: Manganese dioxide, Micro-emulsion technique, Zinc-ion battery.

1. INTRODUCTION

Energy resources push the current techno-sphere of a realm to drive today's society into a new tomorrow's one. They act as a lung for the global modern economy of a country. Issue of economic growth of a country entirely depends on the degree of energy consumption. However, the pattern of unsustainable consumption of non-renewable energy resources such as coal, natural gas, oil *etc.* and subsequent environment deterioration nature have been triggered us to use renewable energy resources (Karden *et al.*, 2007; Tran *et al.*, 2021). Among various sustainable energy resources the availability of solar, wind and water are discontinuous. Because of this intermittent behaviour of solar, wind and water resources scientists around the world are in the quest of effective mediums for storing and transferring energy upon necessity (Panchal *et al.*, 2016; Parker *et al.*, 2017). The development of energy storage devices are an urgent need for the continuous consumption of renewable energy resources. Accordingly, the advent of various types of storage technologies such as lead-acid batteries, nickel-cadmium batteries, lithium ion batteries and nickel-metal hydride batteries have been provided hope and viable solutions associated with renewable resources. The inherent constraints of these mediums have been limited their potential applications in large-scale energy storage systems. Therefore, finding ways to overcome the shortcomings of those battery systems make up aqueous rechargeable batteries device (ARBD). Aqueous solution of salt acts as an electrolyte in aqueous battery. Natures of the aqueous solutions of salt ensure several advantages such as cheapness, high security and environment benignity compared to non-aqueous batteries. In addition, the high ionic conductivity of aqueous solutions of salt greatly improved the rate capability and performance of the ARBD.

So far, many research groups have done their pioneering work in the direction of ARBD. Among these candidates for aqueous rechargeable batteries, aqueous zinc ion batteries (AZIBs) paved outstanding wave of research direction with full of vitality since the first development of Zn/ZnSO₄/MnO₂ system by Yamamoto *et al.* in 1986 (Li *et al.*, 2018). Afterwards, tremendous studies have been made for the development of AZIBs. Some pioneering works have been shown significant advances to achieve high capacity and acceptable energy density of AZIBs. Their successes have been encouraged to develop cathode materials such as manganese-based oxides [Wan *et al.*, 2018], vanadium-based materials (Hao *et al.*, 2019) and Prussian blue analogue (Maccario *et al.*, 2008) for low cost, high safety, long cycle life and environmentally friendly AZIBs with more efforts. Subsequent strategies such as compositing of conductive materials, construction of nanostructure materials, defect introduction and interlayer spacing adjustment of the existing materials have been the hot topics to

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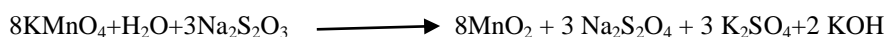
implement the transition of AZIBs from laboratory to commercialization (Li *et al.*, 2017). AZIBs research based on those strategies concern insights to delve many elusive obstacles such as dendrite formation, low coulombic efficiency and poor reversibility (Luo *et al.*, 2017). Strategies to overcome the aforementioned bottleneck for the potential commercial applications inspire us to coat manganese dioxide (MnO₂) using conductive silver (Ag) metal. Compared to MnO₂ electrode material alone, there is a clear benefit to the combination of MnO₂ and metallic Ag in terms of improved electrical conductivity. In this study, core@shell type MnO₂@Ag material has been prepared through the versatile reverse micelle route and applied as cathode material for rechargeable AZIBs.

2. MATERIALS AND METHODS

Materials and chemicals for the experimental operations were bought from a number of chemical companies. The materials and chemicals purchased were all laboratory grade and were used without additional purification. The methodology of the study consists of two parts. At first, core shell MnO₂@Ag materials has been prepared using water in oil micro-emulsion technique and its characterization. Next step consists of the fabrication of CR-2032 coin cell using the prepared MnO₂@Ag material.

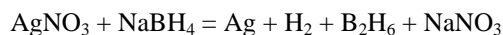
(i) Methodology for the synthesis of MnO₂@Ag material

Triton X-100, cyclohexanol, and cyclohexane were utilized as surfactant, co-surfactant, and oil phase, respectively, in the synthesis of reverse micelles. 20 mL cyclohexane, 12 mL Triton-X 100, and 8 mL cyclohexanol were combined in a beaker in a 5:3:2 ratio to make the micro-emulsion, which was then magnetically stirred continuously until it was transparent. 4 mL water was added to the transparent micro-emulsion solution and stirred for a while. Four stoppered flasks were filled with equal volumes of micro-emulsion solution. In an analytical balance, 0.002 mol Na₂S₂O₃·5H₂O and 0.0053 mol KMnO₄ were weighed, and poured into two separate stoppered flasks containing micro-emulsion. After that, each stoppered flask was magnetically stirred for 1 hour. Na₂S₂O₃·5H₂O incorporated micro-emulsion was then added dropwise into micro-emulsion containing KMnO₄. The resultant mixture was then magnetically stirred for 12 hours to produce MnO₂, resulting in blackish MnO₂. The reaction can be represented by the following equation.



(ii) Preparation of 5% MnO₂@Ag

MnO₂ was initially prepared in micro-emulsion using the process described above. 0.363g AgNO₃ and 0.0081 NaBH₄ was weighed in an analytical balance. Then the weighed AgNO₃ and NaBH₄ were poured into another two separate stoppered flasks which containing micro-emulsion solution. Then micro-emulsion having AgNO₃ was transferred to the flask containing MnO₂ particles. It was then followed by the addition of NaBH₄ from another flask. AgNO₃ was reduced and formed shell over the prepared MnO₂ particles. The reaction was magnetically stir for 12 hours and finally MnO₂@Ag was formed. The reaction between AgNO₃ and NaBH₄ can be represented as follows.



After completing the reaction, the micro-emulsion containing MnO₂@Ag was filtered. The filtered product was dried in the oven for 4 hours. To obtain the final product, the substance was placed in a crucible and calcined at 300°C for 4 hours.

(iii) Methodology for the fabrication of CR-2032 coin cell and its characterization

CR-2032 cell was fabricated as coin cell. In a separately, the cathode electrode was prepared by mixing MnO₂/MnO₂@Ag, carbon black, and polyvinylidene fluoride at the weight ratio of 8:1:1. N-methyl pyrrolidine was used to prepare the slurry of the mixture. The prepared slurry was coated on stainless steel plate and dried at 80°C. 3M ZnSO₄ was used as electrolyte. Filter paper was used as separator. Zinc foil was used as anode. Along with them other components like spacer, ring and case were used to fabricate CR-2032 coin cell. Biologic sp-300 electrochemical workstation was used to study the electrochemical properties such as specific capacity, electrochemical impedance spectroscopy and cyclic voltammetry of the prepared CR-2032 coin cell.

3. RESULTS AND DISCUSSIONS

3.1 X-ray Diffraction Analysis

Figure 1 shows a schematic representation of the micro-emulsion technique utilized to prepare MnO_2 and $\text{MnO}_2@Ag$ materials. KMnO_4 has been encapsulated within the pores of the reverse micelle core in one micro-emulsion. Another reactant, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, was encapsulated within the pores of a reverse micelle core also. MnO_2 was produced after the two reactants were mixed and stirred together. AgNO_3 and NaBH_4 were added to the synthesized MnO_2 encapsulated in the reverse micelle pore to make $\text{MnO}_2@Ag$ core@shell nanoparticles. The reaction mixture was filtered, yielding a brown-colored $\text{MnO}_2@Ag$ product. After that, the product was calcined at 300°C and stored in a vial. At the same reaction conditions, bare MnO_2 (without the addition of AgNO_3 and NaBH_4) was made for comparison. For characterization of the produced MnO_2 and $\text{MnO}_2@Ag$ materials, a number of tests including UV-visible spectroscopy, FT-IR, FESEM, XRD, EDS, and electrochemical characterization were used.

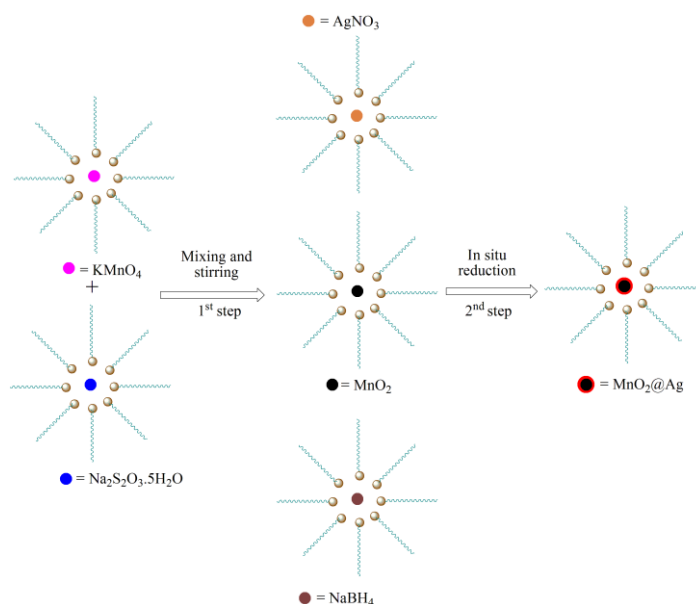


Figure 1: Schematic illustration of the preparation MnO_2 and $\text{MnO}_2@Ag$ core shell nano-materials.

3.1 FTIR-Analysis

The FTIR spectra of MnO_2 within the wavenumber ranges from 400 to 4000 cm^{-1} has been shown in Figure 2. The peak at 522 cm^{-1} , which is attributed to the Mn-O bond, appears to be intensifying (Karnchanawong *et al.*, 2009; Xará *et al.*, 2009). The Mn-O stretching mode can be assigned to the strong absorption band at 522 cm^{-1} , confirming the presence of a Mn-O bond inside the MnO_2 structure.

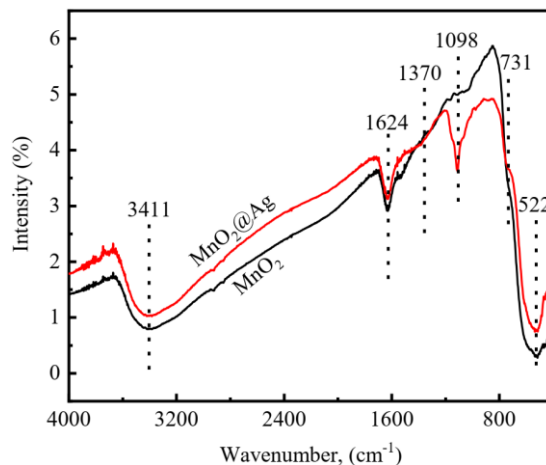


Figure 2: FTIR spectrum shown by the prepared sample.

The O-H bending vibrations combined with Mn atoms correspond to the absorption bands at 731 cm^{-1} and 1370 cm^{-1} . The presence of absorbed water molecules in the MnO_2 (1624 cm^{-1} and 3411 cm^{-1}) structure is suggested by the presence of O-H vibrations in the FTIR spectrum. MnO_2 hydrated characteristics may enrich cation diffusion, hence boosting MnO_2 capacitance (Belardi *et al.*, 2011; Sait *et al.*, 2014).

3.3 XRD-Analysis

Figures 3(a) and 3(b) depict the XRD patterns of the prepared MnO_2 and $\text{MnO}_2@Ag$ materials respectively. The crystalline structure of the two samples was similar, as indicated. The diffraction peaks at $2\theta = 12.7^\circ$, 18.1° , 28.8° , 37.5° , 42.1° , 49.9° , 56.2° , and 60.3° corresponded well with the diffraction peaks of the $\alpha\text{-MnO}_2$ standard data at (110), (200), (310), (211), (301), (411), (600), and (521) (JCPDS card PDF file no. 44-0141). The micro-emulsion method appears to have produced crystalline MnO_2 and $\text{MnO}_2@Ag$ as evidenced by the XRD pattern.

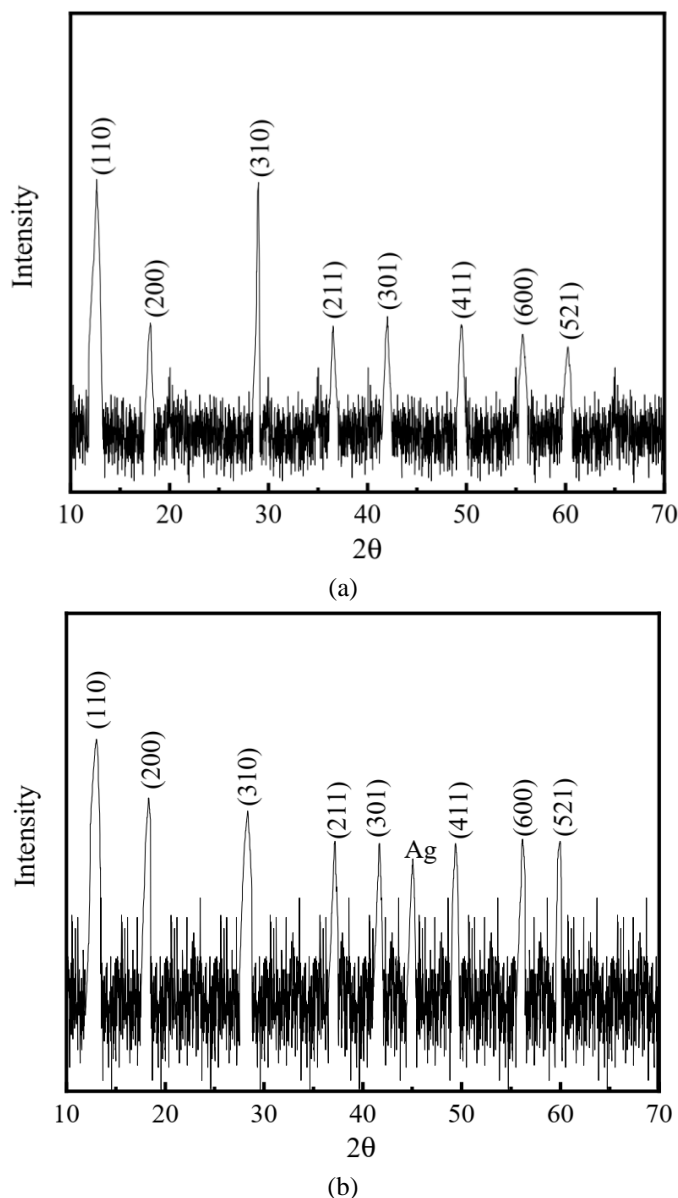
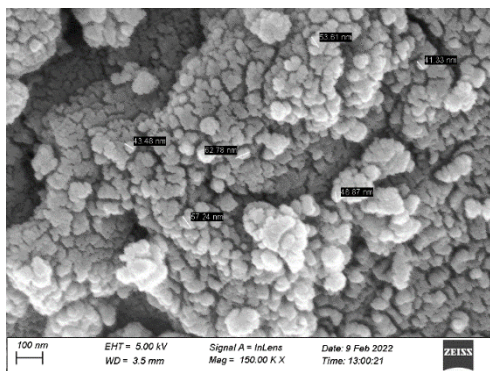


Figure 3: XRD patterns of the prepared (a) MnO_2 and (b) $\text{MnO}_2@Ag$ samples.

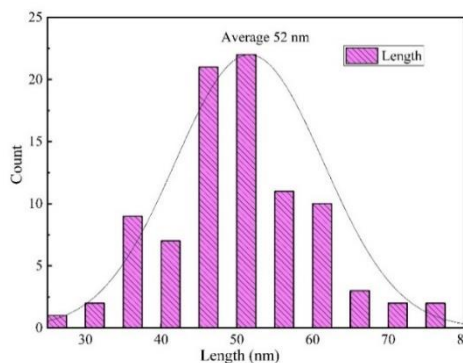
3.4 FESEM Analysis

The shape and particle size of the produced MnO_2 and $\text{MnO}_2@Ag$ materials are investigated using field emission scanning electron microscopy. Figure 4 (a) and (c) illustrates the shape of the prepared MnO_2 and $\text{MnO}_2@Ag$ materials respectively. The corresponding particle size distribution are represented in Figure 4 (b) and (d) respectively. The produced MnO_2 materials are spherical in shape, with an average size of 52 nm, as

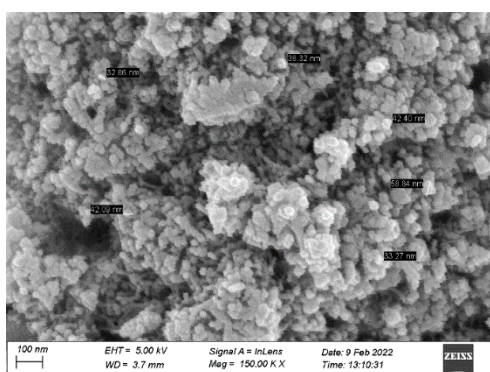
shown in Figure 4 (a). The particles $MnO_2@Ag$, on the other hand, are slightly smaller and have a similar form. From the perspective of an Ag sphere on the surface of MnO_2 materials, this observation makes sense.



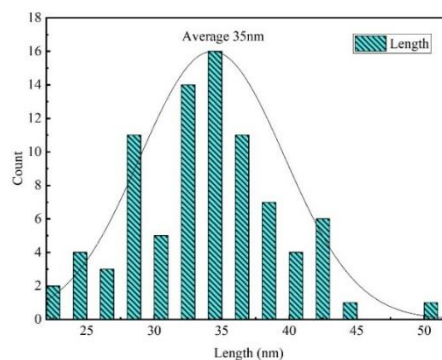
(a) FESEM images of MnO_2



(b) Histogram of image (a)

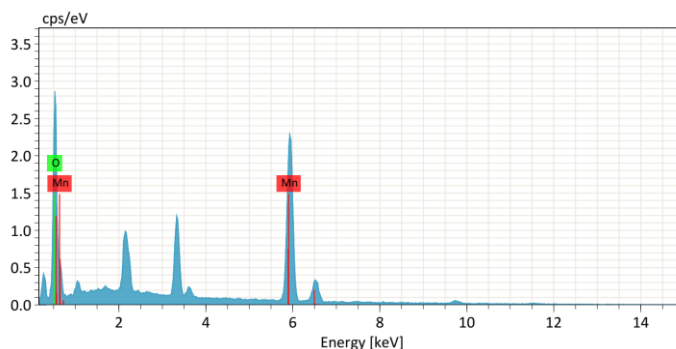


(c) FESEM images of $MnO_2@Ag$

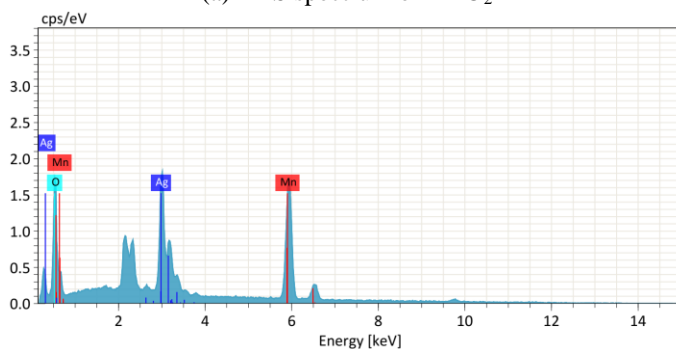


(d) Histogram of image (c)

Figure 4. FESEM images and corresponding histogram of the prepared MnO_2 and $MnO_2@Ag$ materials.



(a) EDS spectrum of MnO_2



(b) EDS spectrum of $MnO_2@Ag$

Figure 5: EDS spectrum of the prepared (a) MnO_2 and (b) $MnO_2@Ag$ materials.

3.5 EDS Analysis

The EDX of the nanoparticles MnO_2 and $\text{MnO}_2@\text{Ag}$ is shown in Figure 5 (a) and 5 (b) respectively. It indicates that the prepared nanoparticles are primarily made up of MnO_2 . In the EDS spectrum 5(b), the element Ag is found. This indicates that the substance $\text{MnO}_2@\text{Ag}$ is manufactured. The remnants of K signal in this image are impurities left over from the reactions. Carbon tap sample holder is responsible for the C signal in this image. Because the elements K and C are present in trace levels in the metal oxide samples, they cannot be detected as new phases in the XRD pattern.

3.6 Electrochemical Characterization

Coin cells were used to test the electrochemical performance of the prepared samples MnO_2 and $\text{MnO}_2@\text{Ag}$ samples. The coin cells CR-2032 were fabricated and tested using the synthesized cathode material. This section goes into the specifics of several electrochemical characterizations.

3.6.1 Cyclic Voltammetry (CV) of CR-2032 Coin Cell Using MnO_2 Cathode Material

The CV curves of the MnO_2 -Zn cell is shown in Fig. 6. An electrochemical window of 1.0-2.1 and a scan rate of 5 mV/s were used to run the cyclic voltammetric scan. At 1.7903 V and 1.2331 V, two pairs of reversible redox peaks can be clearly seen. A two-step reaction can be represented by these two peaks [Zhao *et al.*, 2018 & Sun *et al.*, 2017]. An anodic peak at 1.7903 V and a cathodic peak at 1.2331 V are observed at first cycle of the fresh battery. The phase of Zn^{2+} extraction can be represented by the anodic peak. The cathodic peak can be used to determine the phase of Zn^{2+} insertion. The acquired CV profiles are similar to an approximate those of previously reported $\alpha\text{-MnO}_2$, showing that the synthesized MnO_2 may use the same charge storage mechanism as previously reported $\alpha\text{-MnO}_2$ [Chen *et al.*, 2020 & Gao *et al.*, 2020].

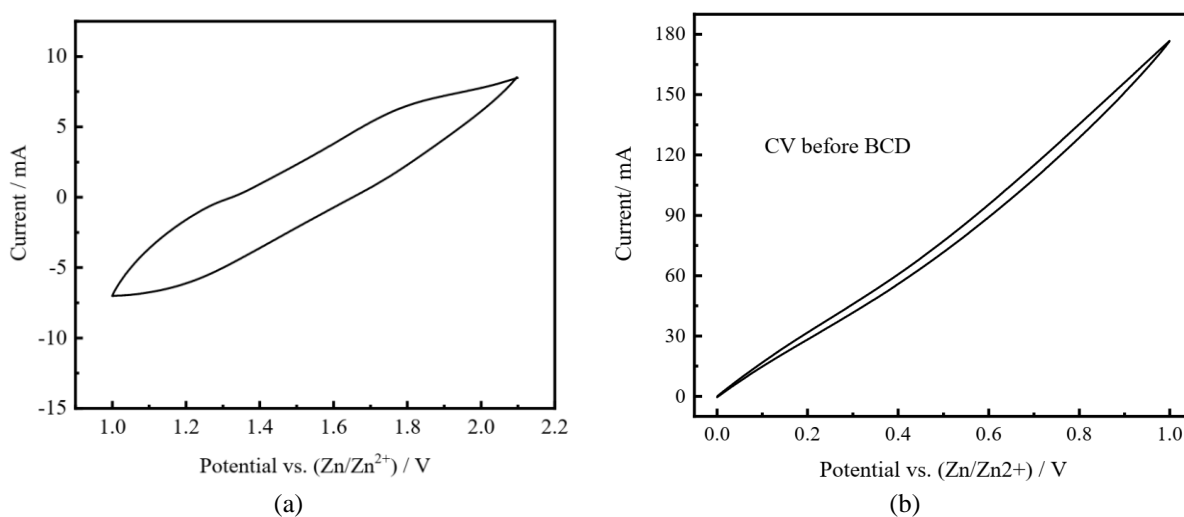


Figure 6: CV plot of coin cell using (a) MnO_2 (b) $\text{MnO}_2@\text{Ag}$ cathode materials at 5 mV/s.

3.6.2 Battery Charge Discharge

Figures 7 (a) and 7 (b) show the cycling performances of MnO_2 and $\text{MnO}_2@\text{Ag}$ samples at 250 μA respectively. The charge/discharge profiles are consistent with the CV profiles as shown in Figure 6. Both type of batteries were cycled up to 20 cycles. MnO_2 and $\text{MnO}_2@\text{Ag}$ samples have initial charge capacities of 126 mAh and 115 mAh, respectively. MnO_2 and $\text{MnO}_2@\text{Ag}$ samples have initial discharge capacities of 140 mAh and 203 mAh, respectively. Hence, $\text{MnO}_2@\text{Ag}$ samples have a larger initial discharge capacity than bare MnO_2 , which can be attributed to the Ag coating on MnO_2 . After 20 cycles, the capacity of MnO_2 batteries has been found to be nearly constant.

After the eighth cycle, however, the charging capacity of Ag coated MnO_2 dropped by 16 % and the discharging capacity dropped by 18 %. Following that, capacity remains nearly constant for the remainder of the cycles. Initially, the Ag coating on MnO_2 can be accountable for the greater charge and discharge capabilities of $\text{MnO}_2@\text{Ag}$. The disintegration of the Ag coating from the MnO_2 surface could explain the sudden attenuation of

MnO₂@Ag after the eighth cycle. Sudden capacity attenuation of MnO₂@Ag may have resulted from the dissolution of Mn from MnO₂. Overall, the MnO₂@Ag electrode has a higher capacity than the MnO₂ electrode.

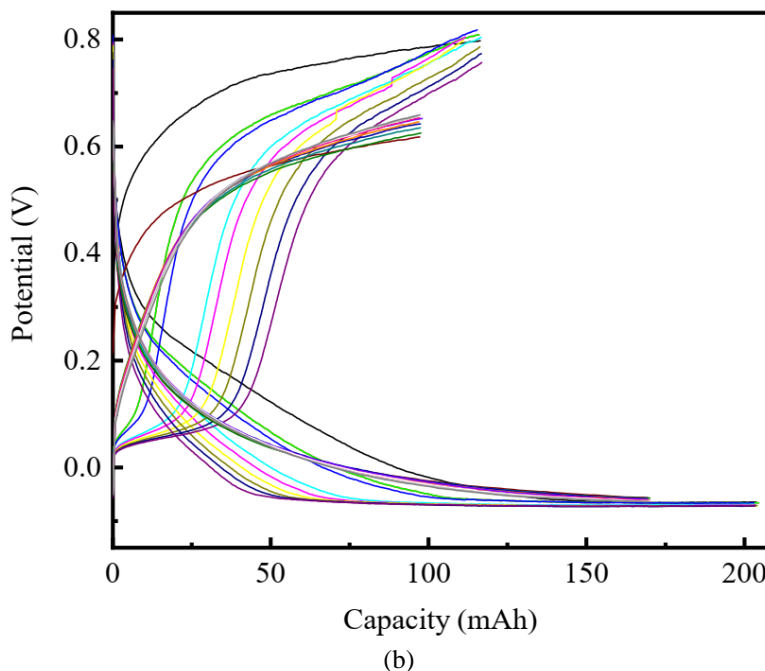
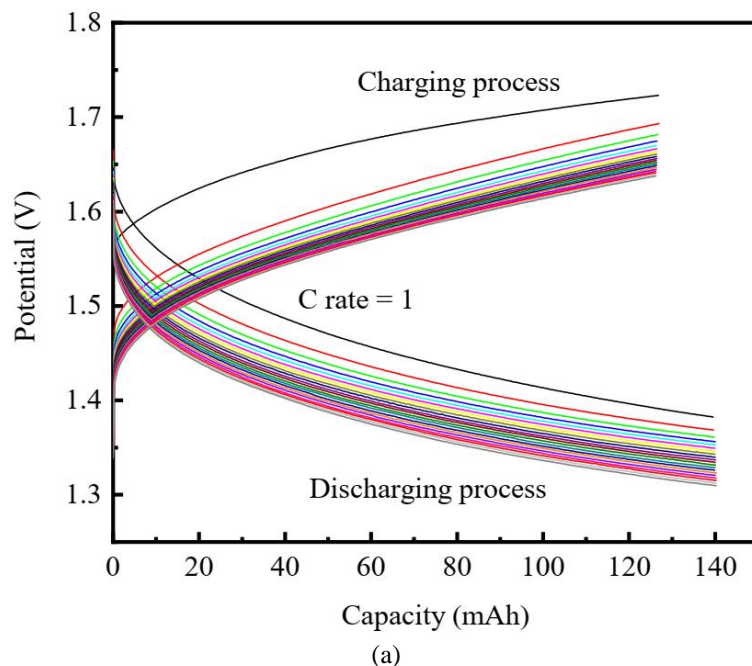


Figure 7: Cycling performances of (a) MnO₂ and (b) MnO₂@Ag samples.

3.6.3 Potenti Electrochemical Impedance Spectroscopy (PEIS) of MnO₂ and MnO₂@Ag

PEIS analysis was used to determine the impedance of MnO₂ and MnO₂@Ag electrodes. PEIS measurements for MnO₂ and MnO₂@Ag electrodes are shown in Figure 8 (a) and Figure 8 (b), respectively. According to the fitting results, the resistance of MnO₂@Ag is lower than that of MnO₂. Before BCD profiles, the R_s value of MnO₂ electrode is 88 ohm. The R_s value of MnO₂@Ag electrode is 37.6 ohm. The reduction in resistance of MnO₂@Ag is due to the Ag coating on the MnO₂ electrode. MnO₂@Ag electrodes with Ag coating may have better electron and ion conductivity. It may have improved wettability and electrode-electrolyte contact surface.

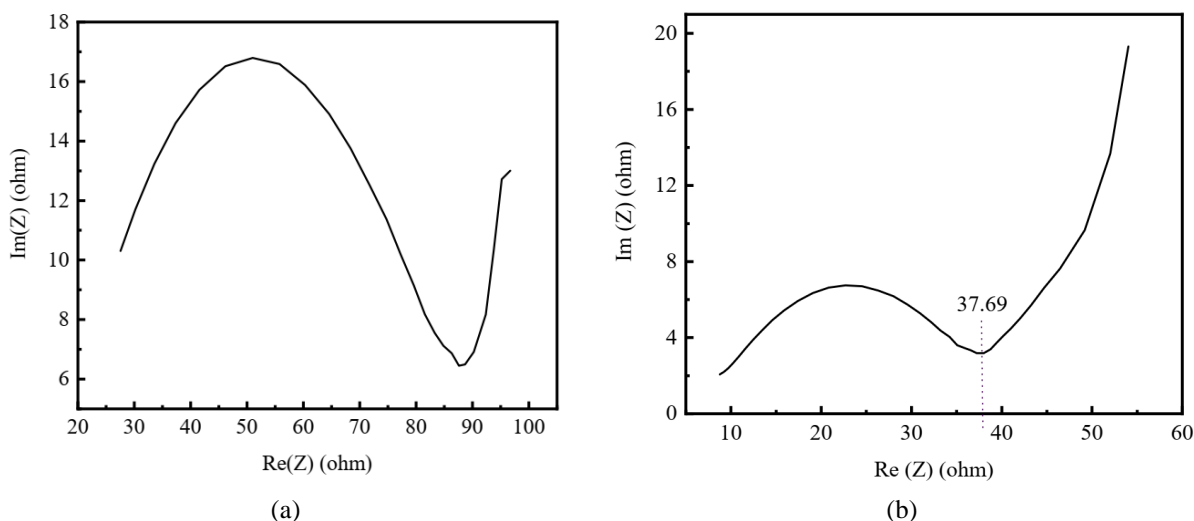


Figure 8: PEIS analysis of CR-2032 coin cell using materials (a) MnO_2 (a) $\text{MnO}_2@Ag$.

4. CONCLUSIONS

This study shows a straightforward, scalable, and cost-effective method for producing MnO_2 and $\text{MnO}_2@Ag$ cathode materials using micro-emulsion technique. The nanostructured MnO_2 and $\text{MnO}_2@Ag$ cathode materials were then characterized and used as cathodes for rechargeable zinc ion batteries. The effect of an Ag coating on the surface of MnO_2 was thoroughly investigated. This study found that Ag coating on MnO_2 nanoparticles can have better electrochemical performance than bare MnO_2 . As a result, Ag coating on MnO_2 is a good technique to create $\text{MnO}_2@Ag$ cathode materials for Zn/ $\text{MnO}_2@Ag$ ARB construction.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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