High Energy Density Rechargeable Battery: Study of Polyvinylpyrrolidone Encapsulated MnO2 Composite as Cathode Material

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Abstract: The availability of an efficient and low cost battery is the key for developing practical electric vehicles (EV). The currently available nickel-metal hydride battery could be a good candidate for EV but it is too expensive and not environmentally acceptable for EV applications. Rechargeable lithium ion batteries that use non-aqueous (organic solvents) electrolytes have been available in the market for over a decade are the most attractive power sources that are vital to meet the challenge of global warming, greenhouse gas emissions and fossil fuel consumption. These can be readily used for powering consumer electronic devices. However, it is quite difficult to make a large lithium battery which is both safe and inexpensive. This is due to the reactivity of the electrode materials with the non-aqueous electrolytes i.e. thermally unstable. In order to realize a perfect safety even at high temperature, non-aqueous (organic) electrolyte may be replaced by aqueous electrolyte system. In the case of non-flammable (aqueous) electrolyte, lithium hydroxide may have an advantage in terms of high conductivity that lowers the charge transfer resistance and cell impedance. The Zn|LiOH|MnO2 battery chemistry reported in this work delivered 142 mAh/g and the cell was rechargeable for multiple cycles. Alternatively, Polyvinylpyrrolidone (PVP) coated MnO2 showed improved discharge capacity of 200 mAh/g but a larger amount of PVP coating causes a decrease in capacity to 83 mAh/g. The incorporation of Bi2O3 + TiS2 (3 wt% each) additives into the MnO2 cathode was found to improve the overall cell performance, this is partly due to the suppression of proton insertion.

Keywords: MnO2; additives; aqueous; battery; rechargeability; polyvinylpyrrolidone (PVP).

Introduction
Recently, we showed that lithium intercalation can occur in manganese dioxide (MnO2) electrode with Zn anode in aqueous rechargeable battery technology developed by the authors at Murdoch University is low cost, environmentally benign and inherently safe [1]. This new (Zn-MnO2) aqueous rechargeable battery technology developed by the authors at Murdoch University is low cost, environmentally benign and inherently safe. However, higher energy density and cyclic life of the Zn|LiOH|MnO2 system are required for exploiting this technology as a better system and compete with other lithium battery counterparts. In this work, two approaches have been made to render higher energy density for aqueous rechargeable battery. One approach is unique synthetic method to carbon coat the MnO2 particles using polyvinylpyrrolidone (PVP) as a source. An electrically conducting polymer, PVP, has excellent wetting properties that make it good as an encapsulation on MnO2 particles [2]. PVP as a polymer can form a conducting matrix and acts as a backbone in the cathode material. This polymer coating on the host MnO2 enhances the conductivity and lithium intercalation mechanism during discharge but unfortunately reduces the working voltage of MnO2 cathode during synthesis. Also, the optimal range of PVP as additive is explored. The second approach is the incorporation of small amounts of TiB2 and Bi2O3 additives (3 wt% each) through physical mixing that found to enhance the capacity without any decrement of voltage. Finally, high energy density of 270 Wh/Kg with good capacity retention that achieved with mixed additives (Bi2O3 + TiS2) on MnO2 is reported in this paper.

Experimental
The γ-MnO2 type (IBA sample 32) material used in this work was purchased from the Kerr McGee Chemical Corporation. Bismuth oxide (Bi2O3), polyvinylpyrrolidone (PVP) was obtained from Aldrich chemical company and titanium disulfide (TiS2) from Alfa Aesar. For PVP assisted MnO2, metal oxide powder (MnO2) was dissolved in water at 80 °C with an effective stirring to obtain a homogenous solution. Then the PVP was added in 1:1 weight ratio to the metal ions. The process of stirring and heating was continued until thick transparent gel was obtained. Then, the gel was dried at 110 °C in hot oven for 10 h. Finally, the product was heated at 275 °C for 3 h in air to get the PVP decomposed.

Results and Discussion
Physical characterization: Figure 1 shows the X-ray diffraction patterns of the samples obtained with polyvinylpyrrolidone (PVP) as a polymer additive in different ratios (wt %) in the parent manganese dioxide (γ-MnO2 type) cathode. In the absence of PVP (Fig. 1a), the diffraction peaks corresponding to the γ-MnO2 phase appears at 2θ = about 22.1°, 37.4°, 42.7° and 56.2° are well defined. These four peaks are indexed as (1 2 0), (1 3 1), (3 0 0) and (1 6 0) respectively, by assuming γ-MnO2 is a non-periodic intergrowth of pyrolusite and ramsdellite structural units [3]. In the presence of PVP ≤ 5 wt% (Fig. 1b-c) the characteristic of the γ-MnO2 phase is intact but at the higher ratios ≥ 5 wt% (Fig. 1d-e) the peaks are poorly defined suggesting a presence of disorder. This implies the
MnO$_6$ octahedral units with [2 x 2] tunnels contain excess polymer, since the synthesis employed PVP as a starting material. The SEM results in Fig. 2b-c indicate that the PVP assisted samples are homogenous with finer particle size as compared to the plain material in Fig. 2a. At higher ratios of PVP (Fig. 2d-e), the particles are found to be bigger and not compact implying a poor electrochemical reaction if applied to electrode material. In Fig. 2b (for 2 wt %) the manganese dioxide and polymer cannot be distinctively observed. This shows the polymer may have been encapsulated nicely on the MnO$_2$ particles enhancing the conductivity and the electrochemical activity of the material. To investigate this, charge-discharge and cyclic voltammetry studies describing the redox mechanism in aqueous electrolyte were carried out on all samples.

**Electrochemical characterization:** Figure 3 shows the difference in the discharge characteristics of Zn-MnO$_2$ aqueous LiOH cells containing plain and PVP assisted (2 wt %) MnO$_2$ as cathode materials. The open-circuit voltage (OCV) of the plain MnO$_2$ (containing no additive) is 1.87 V and the cell discharged at a higher mid voltage of 1.55 V while the PVP assisted MnO$_2$ showed 1.53 V as OCV with a mid discharge voltage of 1.25 V under identical conditions. However, the discharge capacity for the battery with plain MnO$_2$ was 142 mAh/g as compared to 200 mAh/g at the first cycle. The active material utilization of the PVP assisted MnO$_2$ was 30% higher than that for the plain MnO$_2$ material under identical mass composition. To understand the redox behavior, a slow scan cyclic voltammetry has been performed on MnO$_2$ materials. The first cyclic voltammogram of the plain MnO$_2$ can be compared to that of PVP assisted (2 wt %) MnO$_2$ in aqueous LiOH by referring to Fig. 4. The data for both the materials were obtained under identical conditions. The CV’s appear to be quite similar, with the reduction peak for plain and PVP assisted MnO$_2$ occur at -304 and -280 mV respectively. For PVP assisted MnO$_2$, the peak at -280 mV is more intense and reversible indicating capping of PVP on the surface removed the surface traps or defects. Based upon what we have postulated earlier [1], the reduction peak corresponds to the formation of lithium-intercalated MnO$_2$ and the corresponding anodic peak at 92 mV is reverse of this reaction. Figure 3 also shows the reversibility of the Zn-MnO$_2$ materials, both the cells could be reversibly discharged and charged. The two materials

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**Figure 1** X-ray diffraction patterns of the (a) plain MnO$_2$ powder (b) PVP assisted MnO$_2$ powder containing various proportions of PVP (b) 2, (c) 5, (d) 10, and (e) 20 wt.%

**Figure 2** SEM images of (a) plain MnO$_2$ powder (b) PVP assisted MnO$_2$ powder containing various proportions of PVP (b) 2, (c) 5, (d) 10, and (e) 20 wt.% (labeled top to bottom sequentially).
Figure 3 Discharge-charge profiles of a Zn-MnO₂ cell at a constant current (0.2 mA) in LiOH electrolyte illustrating the cells are rechargeable. The cathode containing (a) plain and (b) PVP assisted (2 wt %) MnO₂.

Figure 4 Comparison of the cyclic voltammogram (a) plain and (b) PVP assisted (2 wt %) MnO₂ in saturated LiOH electrolyte. Voltage was swept cathodically initially from +0.2 V to -0.4 V and back at a scan rate of 25 µV s⁻¹.

Figure 5 Cyclability of Zn-MnO₂ battery in the presence and absence of additives. The cathode containing (a) plain (b) PVP assisted 2 wt.% MnO₂ and (c) TiS₂ + Bi₂O₃ (3 wt.% each) added MnO₂ cathode.

Figure 6 Discharge-charge profiles of a Zn-MnO₂ cell at a constant current (0.2 mA) from the PVP assisted MnO₂ with a range of PVP proportions indicated in the profiles.

exhibited quite different rechargeability when subjected to multiple cycles as shown in Fig. 5a-b. The efficiency of the battery containing plain MnO₂ material dropped rapidly while for the PVP assisted battery the decrease in capacity was gradual. At the 25th cycle the available capacity for the plain material is 102 mAh/g and PVP assisted is 176 mAh/g. The observed difference is attributed to the polymer (PVP) as additive. PVP contains nitrogen and oxygen atoms in their molecular structure. The nitrogen dioxide interaction with polymers containing imide groups in the main chains of PVP establishes strong affinity [4] to a single unit of MnO₂ colloid. Hence, the role of PVP is described as (a) the imide and metal bonding controls the particle size by forming passivation layers the MnO₂ core and (b) prevent particle aggregation due to the repulsive force acting among the polyvinyl groups. While the addition of larger amount of PVP ≥ 5 wt% on the MnO₂ surface may cause an attraction between the polymeric chains leading to destabilization. This is reflected in the electrochemical behavior of PVP assisted samples showed in Figures 6-7. The initial discharge-charge behavior of the PVP assisted MnO₂ with different ratios are carried out at a constant current of 0.2 mA is shown in Fig. 6. Increasing the polymer source over 5 wt% causes the decrease in the discharge-charge capacity. As discussed in the XRD and SEM results, a part of PVP may be incorporated into the [2 x 2] tunnel in the MnO₂ structure. This would hinder the lithium insertion into the structure, resulting in a lower material utilization of 83 and 37 mAh/g for 10 and 20 wt% PVP (in Fig. 6). The discharge capacities (for PVP ≥ 5 wt%) also decreased rapidly upon cycling denoting the degradation of the crystal structure. The lithium intercalation and de-intercalation mechanism was severely hindered for the larger amount of PVP added MnO₂ as evidenced in Fig. 7c-d.
Cyclic voltammogram of MnO₂ with a range of PVP contents (a) 2, (b) 5, (c) 10 and (d) 20 wt. %.

Discharge-charge curves of TiS₂ + Bi₂O₃ (3 wt. % each) added MnO₂ cathode.

The coated PVP on the MnO₂ layer facilitate the reduction reaction mechanism leading to an increase in discharge capacity (Fig. 6) and well-defined redox peaks (2 and 5 wt% in Fig. 7a-b). Although the objective is achieved, in terms of higher discharge capacity of 200 mAh/g but the lower discharge voltage of 1.2 V is a drawback for PVP as a source, which may be difficult to compete with the current battery benchmark. As detailed in the introduction section, small amount of an incorporation of additives through physical mixing in the MnO₂ cathode provided an important advantage in terms of energy density. An early development of this approach was initiated at the Ford Motor Company [5]. Subsequent to this, several other researchers [6-7] have focused on additives in the MnO₂ cathode material but all their work was mainly restricted to primary batteries. Our group showed a range of additives suitable for aqueous secondary batteries [8-9]. During the cell discharge in LiOH media, mechanism involves both lithium and proton intercalation into the host MnO₂ compound. The intake of proton insertion results in manganese oxyhydroxide (MnOOH) as the discharged product. The MnOOH in the electrode undergoes a dissolution reaction that releases Mn³⁺ ions into the electrolyte. The Mn³⁺ species are further reduced to a soluble Mn²⁺ that subsequently precipitates to form the end products such as Mn₃O₄ and Mn(OH)₂. Interestingly, our studies showed here that the incorporation of additives such as TiS₂ and Bi₂O₃ compounds in a equal proportion (3 wt%) into the MnO₂ cathode retard this disproportionation reaction of Mn³⁺ by keeping the Mn³⁺ ions in the solution for a longer time and thereby prevent the formation of unwanted Mn₃O₄ and Mn(OH)₂. This leads to an enhanced discharge capacity of 187 mAh/g (similar to PVP assisted MnO₂ in Fig. 3b) with improved mid discharge voltage of 1.45 V (Fig. 8). At the 25th cycle the discharge capacity for multiple additives (Bi₂O₃ + TiS₂) was just lowered to 173 mAh/g, reflecting only 8% loss (Fig. 5c). Hence, the multiple additives enhanced the lithium intercalation with an improved capacity while preventing the formation of non-rechargeable products.

Conclusions

On a unique synthetic approach, PVP has been capped on the MnO₂ particles providing a significant influence on the morphology while controlling the particle aggravation. At a lower amount of PVP the discharge capacity of the battery increased to 200 mAh/g but the discharge voltage was lowered. However, the multiple additives (Bi₂O₃ + TiS₂) into the MnO₂ electrode restrain the unwanted discharge products that improved the rate capability of the battery as well as extending the usable lifetime. The cell that contains multiple additives (Bi₂O₃ + TiS₂) has potential application in battery packs with a single cell providing around 1.5 V comprising 270 Wh/Kg.

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