



Electrochemical characterization of an aqueous lithium rechargeable battery: The effect of CeO₂ additions to the MnO₂ cathode

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ARTICLE INFO

Article history:

Received 13 November 2008

Accepted 30 December 2008

Available online 10 January 2009

Keywords:

Battery

Aqueous solution

MnO₂

Additive

CeO₂

Capacity fade

ABSTRACT

The effect of CeO₂ additions on an aqueous rechargeable lithium battery has been investigated. The CeO₂ additions (0, 2, and 5 wt.%) were made to the manganese dioxide (MnO₂) cathode of a cell comprising zinc as an anode and an aqueous saturated lithium hydroxide solution as the electrolyte. The CeO₂ enhances the performance of the cell in terms of capacity and resistance to capacity fade with cycling. This effect is only evident after the first charge cycle. The mechanism by which this occurs may be due to suppression of the oxygen evolution reaction during charging. This results in full reversion of the products of discharge (principally Li_xMnO₂) to MnO₂ during charging, and suppresses the formation of non-rechargeable oxyhydroxides. CeO₂ additions of 2 wt.% were found to be most effective, since additions at the 5 wt.% level caused a decrease in capacity during long-term cycling. This could be due to a synchronizing effect. The effect of additions of a rare earth oxide (CeO₂) and an alkaline earth oxide (CaO) on the electrochemical behavior of the cell is also compared and discussed.

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1. Introduction

Manganese dioxide is considered to be an important component of battery technology [1]. Rechargeable lithium-ion batteries with non-aqueous electrolytes that use manganese dioxide (MnO₂) as a cathode active material can be used for powering consumer electronics. However, these batteries have been subject to safety concerns caused by overheating following internal short circuits. This is due to the reactivity of the battery employing non-aqueous solvents as an electrolyte [2].

The ionic conductivity of non-aqueous electrolytes is about two orders of magnitude lower than an aqueous counterpart. Therefore electrodes must be made thin in order to develop sufficient power. To overcome some of these limitations, we have demonstrated that lithium intercalation/extraction can occur when using an aqueous electrolyte (saturated lithium hydroxide) with zinc as an anode. This cell was shown to be rechargeable [3–5]. However, careful physical characterization of the cell showed that not only lithium, but also hydrogen, shuttled between the MnO₂ cathode and the Zn anode during the cycling. This resulted in a mixture of discharged products including lithium intercalated manganese dioxide and manganese oxyhydroxides. The latter products are non-

rechargeable and reduce the battery capacity on cycling. In our previous publications we investigated a variety of additives (TiB₂ [3]; TiS₂ [4], Bi₂O₃ [5]) which could suppress the formation of non-rechargeable products and enhance the performance of the battery.

Very recently we carried out a microstructural and spectroscopic investigation into the influence of rare-earth oxide (CeO₂) additions [6]. In this paper, the objective is to explore the effect of such additions on the electrochemical behavior including the cycling performance. Of particular interest is understanding the mechanism by which CeO₂ influences the cycling behavior. We have therefore investigated the effect of a range of CeO₂ additions (0, 2 and 5 wt.%) to the MnO₂ cathode to determine the optimum loading. We have also compared this behavior with similar additions of an alkaline earth metal oxide (CaO). The alkaline earth metal hydroxide and/or carbonate helps to suppress or minimize the increase in the internal impedance of the battery which occurs during discharge [7].

2. Experimental

The EMD (electrolytic manganese dioxide; γ -MnO₂) type (IBA sample 32) material used in this work was obtained from the Kerr McGee Chemical Corporation. Cerium oxide (CeO₂) and Calcium Oxide (CaO) were obtained from the Aldrich chemical company. For the electrochemical tests, pellets were prepared by mixing 70–75 wt.% MnO₂ consisting of 0, 2 and 5 wt.% CeO₂ respectively with 20 wt.% acetylene black (A-99, Asbury, USA) and 5 wt.% poly (vinylidene difluoride) (PVDF, Sigma–Aldrich) binder in a mortar and pestle. In the case of CaO modified MnO₂, 73 wt.% MnO₂, 2 wt.% CaO 20 wt.% acetylene black and 5 wt.% binder were used. An electrochemical cell was constructed with the disk-like pellet as the cathode, Zn

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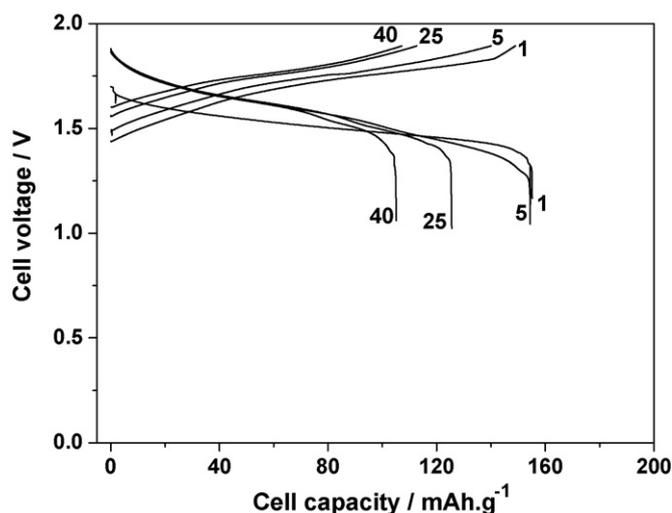


Fig. 1. Multiple discharge–charge behavior of an unmodified MnO_2 cathode (0 wt.% additive). The capacity of the cell decreases on cycling—cycle numbers shown.

metal as the anode and filter paper as the separator. The electrolyte was a saturated solution of lithium hydroxide (LiOH) containing 1 mol L^{-1} zinc sulphate (ZnSO_4) with a pH equivalent to 10.5. The cell design and its experimental details were similar to those reported earlier [3–5].

3. Results

The multiple galvanostatic discharge–charge behavior of the CeO_2 modified (0, 2 and 5 wt.%) MnO_2 cathodes are shown in Figs. 1–3 respectively. The cells were discharged and charged at a constant current density of 0.5 mA cm^{-2} with the lower and upper cut-off voltages of 1.0 and 1.9 respectively. The first discharge capacity of the unmodified MnO_2 cell (0 wt.% additive in Fig. 1) was 152 mAh/g and its corresponding charge capacity was 150 mAh/g . This shows that the cell could be reversibly discharged and charged. The multiple discharge and charge cycles of this material shows that the reversible capacity of about 150 mAh/g was achieved for the first five cycles. After further cycling the efficiency of the cell dropped to 125 and 104 mAh/g following the 20th and 40th cycles corresponding to a 17% and 30% loss in capacity respectively. Although this material is rechargeable the fade in capacity is significant on cycling.

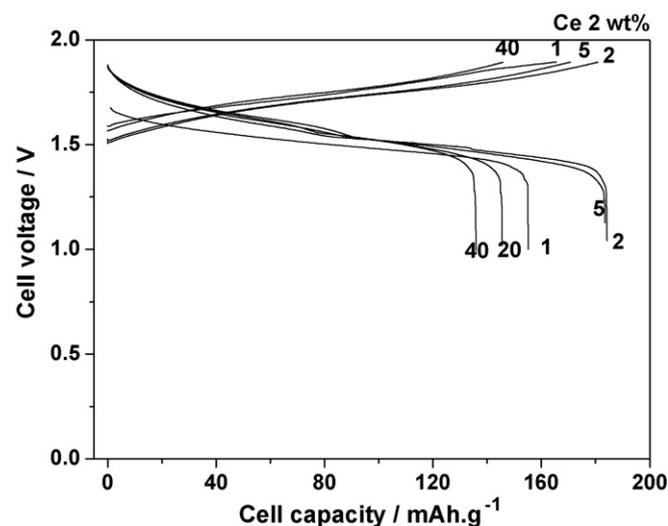


Fig. 2. Multiple discharge–charge behavior of a CeO_2 modified (2 wt.%) MnO_2 cathode. The striking behavior here is the 22% increase in capacity between the 1st and 2nd cycles.

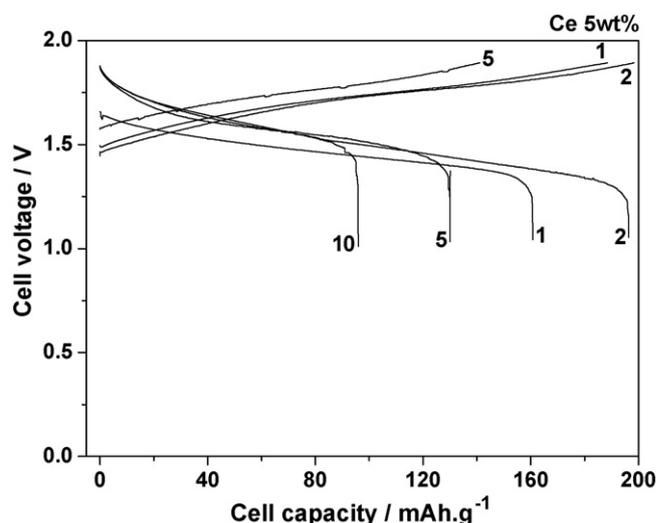


Fig. 3. Multiple discharge–charge behavior of a CeO_2 modified (5 wt.%) MnO_2 cathode. The capacity fades much more quickly on cycling.

In an attempt to suppress the capacity fade, cerium oxide (CeO_2) was added to the MnO_2 cathode. In general, introduction of an additive seems to help stabilize the MnO_2 structure [8–10]. In this regard, we have chosen cerium oxide as an additive and the discharge–charge cycles are shown in Figs. 2 and 3 for 2 and 5 wt.% CeO_2 loading respectively. The capacity of the CeO_2 (2 wt.%) modified cell at the first discharge was 155 mAh/g (Fig. 2). This compares with 152 mAh/g for the unmodified cell (Fig. 1). This shows that the effect of 2 wt.% addition of cerium oxide on the initial discharge behavior is negligible. The charge capacity on the first charge cycle was (160 mAh/g), which shows that the CeO_2 modified cell is fully reversible. However, on the second discharge cycle of the CeO_2 modified cell, the capacity increased from 155 to 190 mAh/g . This indicates that utilization of the material was 22% higher than that of the first cycle. The SEM morphology (Fig. 4) of these discharged materials i.e. unmodified (0 wt.% CeO_2) and CeO_2 modified (2 wt.% CeO_2) cathode of the second discharge cycle samples, highlights some differences between the two materials. The small crystalline like particles of $5\text{--}10 \mu\text{m}$ diameter observed in the unmodified material (Fig. 4a) may correspond to a MnOOH or $\text{Mn}(\text{OH})_2$ whereas for the 2 wt.% CeO_2 modified cathode (Fig. 4b) these particles are less apparent. After multiple discharge cycles (5th cycle) the discharge capacity of the 2 wt.% modified cell (Fig. 2) was still higher (183 mAh/g) than the first discharge capacity of the unmodified cell (152 mAh/g). The discharge capacity of the 2 wt.% CeO_2 modified cell after 20th and 40th cycles were 145 and 135 mAh/g respectively (Fig. 2). These values were 16 and 30% higher than the respective corresponding values for the unmodified cell (Fig. 1).

The role of cerium oxide as an additive was unclear since if it takes part in the reduction/oxidation processes then the first discharge capacity of the CeO_2 modified material should be higher than the unmodified material. However, that is not observed in Fig. 2. For the cell with 5 wt.% CeO_2 additions, the first and second discharge capacities were 160 and 190 mAh/g respectively (Fig. 3). These values were very similar to those seen in the 2 wt.% CeO_2 modified material (155 and 190 mAh/g respectively) (Fig. 2). Increasing the level of CeO_2 additions from 2 to 5 wt.% did not result in any significant changes in the early stage electrochemical behavior. In our previous studies on various additives, we have also found that exceeding a threshold level of additive either offers no further improvement in performance or may in fact degrade it [3–5]. Although the 5 wt.% modified material early electrochemical behavior was comparable to that of the 2 wt.% material, the longer-term

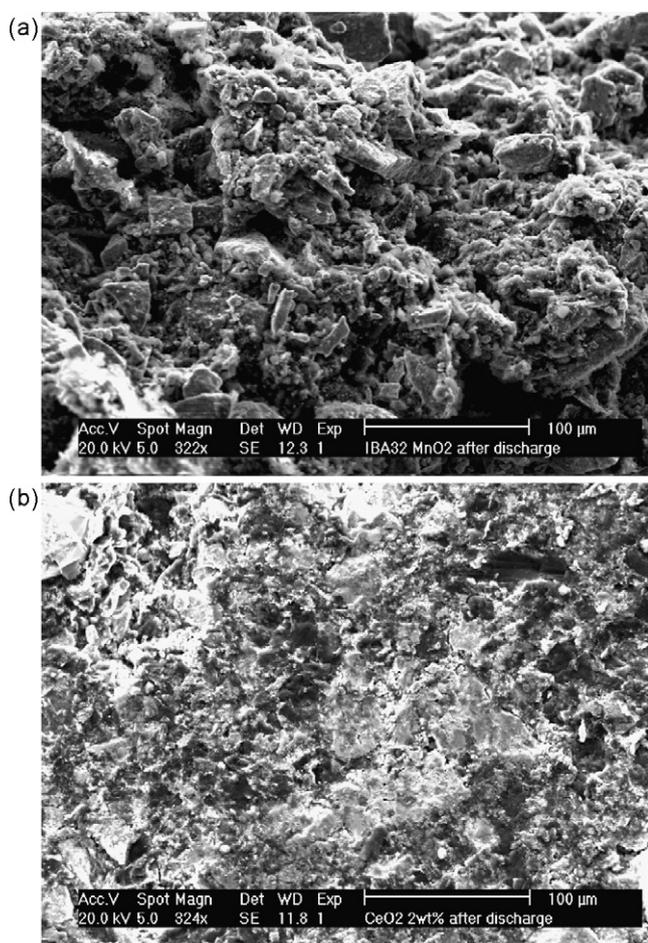


Fig. 4. SEM images of the CeO₂ modified MnO₂ (a) 0 wt.% and (b) 2 wt.% CeO₂ loading, following the second discharge cycle.

cycling behavior was much poorer. The discharge capacity of the 5 wt.% modified cell after the 10th cycle was only 96 mAh/g (Fig. 3), corresponding to a loss of 40% of the initial capacity. The equivalent capacity loss for the 2 wt.% modified material was only (14%). This could be explained in terms that the available amount of active MnO₂ material itself decreased by 5 wt.%. The results of microscopy and spectroscopic investigations on the CeO₂ modified material are reported elsewhere [6].

4. Discussion

In the case of an aqueous system, it is widely reported [11–13] that the charging efficiency of the positive electrode and its utilization is affected by the oxygen evolution process



While charging, a portion of the charge current is consumed by the oxygen evolution reaction, as shown in equation [1]. This oxygen evolution reaction is normally expected to occur while charging and increases with increased charging voltage. Therefore, during charging of the unmodified MnO₂ (0 wt.% additive) if part of the charging current is utilized by the undesired oxygen evolution reaction this may cause some of the discharged MnO₂ material to be retained, i.e. it does not revert to active MnO₂. This would give rise to a gradual capacity fade as seen in Fig. 1.

The presence of the, CeO₂ additive can suppress the oxygen evolution reaction [14] by increasing the electrochemical overpotential for oxygen evolution. This suppression of unwanted reactions

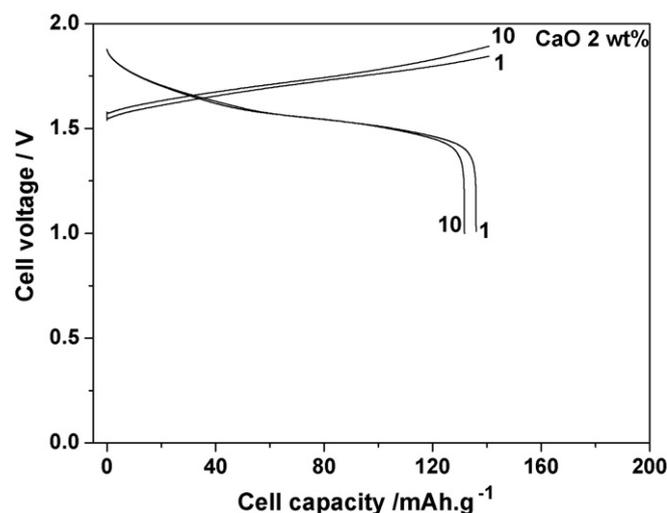


Fig. 5. Multiple discharge–charge behavior of CaO modified (2 wt.%) MnO₂ cathode. The CaO suppresses the formation of non-electroactive forms of manganese resulting in very little change in capacity during cycling. Unlike with CeO₂ additions, no capacity increase is seen.

would improve the coulombic efficiency and could enable a greater degree of conversion of the discharged cathode back into active MnO₂. The CeO₂ additions result in significantly improved battery performance from the second cycle onwards with a 22% increase in capacity after the first charge. However, increasing the CeO₂ levels from 2 to 5 wt.% produced no increase in the capacity beyond that seen for the 2 wt.% material. This could be due to a synchronizing effect between the additive and the active material.

To better understand the role of CeO₂, an alkaline earth metal oxide (CaO) was added to the MnO₂ cathode at 2 wt.% loading—which appeared to be the optimum for CeO₂ additions. The multiple discharge–charge cycles of the CaO modified material are shown in Fig. 5. The CaO modified cell appears to be fully reversible on cycling and the behavior on the subsequent discharge cycle appears quite different from that observed with cerium oxide additions. Unlike the CeO₂ modified material (Fig. 2), which showed a 22% increase in capacity after the first charge cycle, the capacity of the CaO modified material changed very little between cycles 1 and 10 (Fig. 5). Capacity fading is usually accompanied by an increase in the internal impedance of the battery during cycling [7,15] but the presence of CaO additive clearly suppressed this. The behavior of CaO is similar to that observed for a range of other additives (TiB₂ [3]; TiS₂ [4], Bi₂O₃ [5]), in that the formation of non-electroactive forms of manganese are suppressed. However, it is very different to that observed for CeO₂, whereby an increase in capacity resulted from suppression of the unwanted oxygen evolution reaction.

5. Conclusions

The electrochemical behavior reported here shows that the effect of rare earth oxide (CeO₂) additions to MnO₂ enhances the performance of the cell. The first discharge cycle of the CeO₂ modified (2 wt.%) MnO₂ was almost identical to that of an unmodified cell. However, in the second discharge cycle, the capacity of the CeO₂ modified cell increased by 25%. It is believed that the undesirable oxygen evolution reaction is suppressed in the presence of CeO₂. This improves the coulombic efficiency and provides a greater driving force to convert the discharge products back into active MnO₂. Increasing the CeO₂ levels above 2 wt.% causes a decrease in cell capacity on long-term cycling. CaO (2 wt.%) additions behave differently to CeO₂ in that the formation of non-electroactive forms

of manganese is suppressed, in much the same way that we have seen for other additives. This improves the long term cycling ability, by reducing capacity fade. However, unlike CeO₂, CaO additions did not result in any increase in the initial discharge capacity.

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