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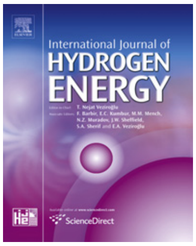

Anodic behavior of zinc in Zn-MnO_2 battery using ERDA technique

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ABSTRACT

The commercial, alkaline zinc-manganese dioxide (Zn-MnO_2) primary battery has been transformed into a secondary battery using lithium hydroxide electrolyte. Galvanostatic discharge–charge experiments showed that the capacity decline of the Zn-MnO_2 battery is not caused by the MnO_2 cathode, but by the zinc anode. The electrochemical data indicated that a rechargeable battery made of porous zinc anode can have a larger discharge capacity of 220 mAh/g than a planar zinc anode of 130 mAh/g. The cycling performance of these two anodes is demonstrated. Structural and depth profile analyses of the discharged anodes are examined by X-ray diffraction (XRD) and elastic recoil detection analysis (ERDA) techniques.

1. Introduction

The emerging trends towards miniaturisation, portability and requirements for high rate capability in electric appliances have motivated an increased demand for rechargeable cells that are low cost and environmentally friendly. Apart from economic and environmental considerations, two of the factors that determine the success of a battery system are rate performance and energy content [1].

Among the various available rechargeable batteries on the market, it is very likely that zinc-manganese dioxide cells have certain advantages in high energy content and low cost. The zinc electrode, due to its high energy per unit volume and high hydrogen overpotential is a very suitable anode material for use in aqueous systems [2]. On the cathodic side, manganese dioxide has for many years found widespread use as a cathode material in aqueous and non-aqueous cells [3]. The zinc electrode, like MnO_2, is a very versatile electrode that can operate in many different electrolytes. It is expected that the demand for this alkaline cell (Zn-MnO_2) will find a niche in the market as the use of toxic lead-acid and nickel–cadmium cells becomes restricted. Zn-MnO_2 systems could replace lithium batteries in many applications. These advantageous characteristics, combined with the disposal problems encountered with primary Zn/MnO_2, have prompted considerable efforts to develop a secondary system. We showed in our earlier publications [4] that primary Zn-MnO_2 can be transformed into a secondary Zn-MnO_2 capable of high rate by replacing traditional potassium hydroxide (KOH) with lithium hydroxide (LiOH) as an electrolyte.

Our work indicated that the cell discharge mechanism involves both lithium and proton intercalation into the host

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MnO_2 compound. In order to improve aqueous rechargeable battery performance in terms of cycle life and voltage profile, we have researched a range of additives [5–8] by physical admixture into MnO_2 cathode. These additives were shown to suppress unwanted non-rechargeable products like MnOOH, Mn_3O_4 and Mn_2O_3 [9,10] resulting in a good battery performance. The high rate performance of this battery still needs to be improved in order to be suitable for a range of new power demanding electronic devices. In the secondary Zn-MnO_2 system, battery performance depends primarily not only on cathode but on the zinc anode to a greater extent. The problems of the zinc anode which we lately discussed in one of our works [11] are irregular dissolution during the discharging period and the uneven zinc deposition during the charging period in the course of repeated cycles.

As zinc has been a promising anode material for battery applications that are widely used in military and commercial applications [2], we have aimed to improve the performance of this material in the present work. From a battery perspective, the properties of electrodes (like effective surface area, porosity and electrical conductivity), separator material, and amount and composition of electrolyte are all pivotal. Various approaches have been attempted to improve the performance of zinc anodes such as impact of size distribution in zinc alloy powders [12], using zinc in form of fibres [13] or gel [14], mixing the zinc electrode with polymer additives [15] or the effect of surfactant as additive in the electrolyte concentration [16]. However, the problem of zinc passivation associated with the dissolution–precipitation mechanism that occurs at the surface on planar/porous zinc electrode is not widely reported. To overcome this issue, in this paper, we have employed two different types of zinc anodes which differ in surface area such as planar and porous. The planar zinc has a low surface area (1 m^2/g) and the porous zinc has a high surface area (6 m^2/g). We have examined the influence of these anodes on the discharge capacity and reversibility of cathodic cell reaction. In order to gain a greater understanding of the effects of these anodes, the discharged zinc anodes have been studied by means of X-ray diffraction (XRD) and elastic recoil detection analysis (ERDA). The ERDA technique is one of the most powerful ion beam techniques for quantifying and depth profiling, with high sensitivity for light elements [17]. It has been widely used in the determination of hydrogen in the near-surface region and it has been found to be a fast, reliable and non-destructive method. The electrochemical performance of the Zn-MnO_2 cell has been examined by galvanostatic discharge–charge experiments.

2. Experimental

The EMD (electrolytic manganese dioxide; γ-MnO_2) type (IBA sample 32) material used in this work was purchased from the Kerr McGee Chemical Corporation. For the electrochemical test, a pellet was prepared by mixing 75 wt% MnO_2 with 20 wt% acetylene black (A-99, Asbury, USA) and 5 wt% poly (vinylidene difluoride) (PVDF, Sigma Aldrich) binder in a mortar and pestle. An electrochemical cell was constructed with a disk-like pellet as cathode, metallic zinc in (powder) porous or (foil) planar form as anode and filter paper as 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 [5,6].

The structural determination and depth profile analysis of the oxidised zinc electrode was examined by X-ray diffraction and elastic recoil detection analysis (ERDA) techniques. For X-ray analysis, a Siemens D500 X-ray diffractometer 5635 using Co-Kα radiation was used. The voltage and current were 40 kV and 30 mA. The scan rate was 1 degree per minute. Two theta values were recorded between 30 and 55 degrees. ERDA measurements were made on a 10 MV tandem ion beam accelerator using a 35 MeV Cl^{5+} ion beam, with re-coiled particles being detected at 45 degrees. The forward-recoiled atoms were mass-analysed using a time-of-flight detection system. The coincidence event map was projected onto the time axis and the depth profile of elements was derived by first principles calculations.

3. Results and discussion

Typical galvanostatic discharge curves of the MnO_2 cells with the LiOH electrolyte employing porous and planar zinc electrodes are shown in Fig. 1. The cells were discharged and charged at a constant current density of 0.5 mA/cm^2 with lower and upper cut-off voltages of 1.0 and 1.9 V respectively. The open circuit voltage for both cells has reached higher than 1.6 V. It can also be seen that well-defined discharge curves were obtained for both cells with calculated discharge capacities of 220 and 130 mAh/g obtained per gram of MnO_2 mass for the porous and planar zinc electrodes respectively. It is also noted that for the porous cell, a plateau is seen around 1.4 V in the discharge curve (Fig. 1a), while for the planar cell it is observed around 1.5 V (Fig. 1b). After the gradual fall of the voltage mainly attributed to the potential decay of the MnO_2 cathode, a rapid drop in potential is observed at the end of the discharge of the planar cell. The porous cell had a high material utilization of 71% while the planar cell had a utilization of only 42% of the theoretical one-electron capacity of MnO_2. The difference seen is attributed to the porous and planar structures of the electrode. Hence, it is clear that the best discharge performance is obtained from the porous zinc electrode for the initial first cycle. Both cells are found to be reversible (Fig. 1) without any significant fade in capacity. The corresponding charge capacity for porous and planar electrodes was 225 and 140 mAh/g respectively.

The second discharge cycle of the porous zinc cell (Fig. 1a) showed that the efficiency of the cell dropped from 220 to 130 corresponding to a loss of 40%. The second charge cycle of the porous zinc cell (Fig. 1a) showed that the efficiency dropped from 225 to 110 mAh/g corresponding to a loss of 52%. This shows that although the porous cell is rechargeable the decline in capacity is significant on cycling. As it is not suitable for a battery application, further cycling was not performed on the porous cell.

The multiple discharge and charge cycles for the planar cell (Fig. 1b) showed outstanding performance. The reversible discharge and charge capacity after the 20th cycle is about 102 and 95 mAh/g reflecting a loss of only 25 and 30%, respectively.