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Relationship of cathode pore-size distribution and rated capacity in Li/MnO_2 cells

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Abstract

An improved MnO_2 cathode has been evaluated. It was found that the high porosity and the pore-size distribution (macropores with a diameter >2000 Å representing >25% of the total pore volume) of the electrode are two determinant factors in performing a high (80%) utilization of the Li/MnO_2 at high discharge rate.

Introduction

Primary Li/MnO_2 cell is one of the most early commercialized Li cells [1]. In general, Li/MnO_2 cells were designed for low current discharge applications due to the safety and cathode rate capability. Recently, there has been an increase in demand for high power, high specific energy sources for many applications such as portable computer, portable power tool, industrial and medical instruments, etc. Li/MnO_2 cells became a candidate for such applications. In order to enhance the Li/MnO_2 cell's power performance, an improved MnO_2 cathode is required [2].

A correlation was found between the electrochemical performance of MnO_2 cathode in nonaqueous electrolytes and their physicochemical characteristics in button cells (3–7). This paper reports the studies of the dependence of the MnO_2 cathode utilization at high rate discharge on the electrode porosity and pore-size distribution. These results can be used to improve the design of the MnO_2 electrodes for enhancing high rate performance of the Li/MnO_2 cells.

Experimental

The Li/MnO_2 cells studied are of a spiral-wound type construction. The test cathodes were prepared by pasting 5.5–5.7 g of the mixture (87 wt.% MnO_2, 5 wt.% carbon black, 5 wt.% graphite and 3 wt.% Teflon binder) onto a stainless-steel Exmet. The cathode preparation and cell assembly were carried out in a dry room with moisture content of less than 2%. Electrolyte used is 1 M $LiClO_4$ in propylene carbonate: dimethoxyethane (PC:DME) (1:1 ratio). The water content of the electrolyte is less than 40 ppm. Celgard microporous polypropylene separator was used in the cells.

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The test cells were designed to be cathode limited. Constant current discharge mode was used to test the cells at room temperature. The capacity and the utilization of the cathodes were determined based on 1.5 V cutoff voltage.

Helium adsorption method (Quantachrome Co., stereopycnometer) was used to determine the porosity of the cathodes. The pore-size distribution of the cathodes was measured by a mercury porosimeter (Quantachrome Co., autoscan porosimeter).

Results and discussion

Figures 1 and 2 illustrate the effect of electrode porosity on the electrode utilization of an 'AA'-size Li/MnO_2 cell as a function of MnO_2 electrode porosity (30 to 60%) at three different high rate discharge currents (24, 40, and 80 mA). The results show that the MnO_2 electrode utilization increases with increasing electrode porosity. Interestingly, there is a distinct, sharp increase in MnO_2 utilization at 40% electrode porosity for cells discharged at 24 mA (Fig. 1). Figure 2 also shows MnO_2 utilization

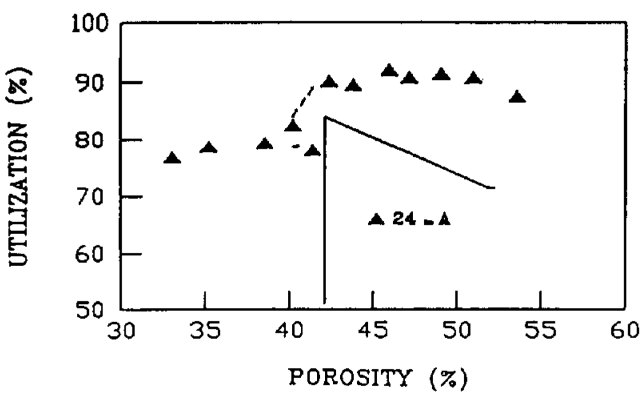

Fig. 1. Relationship between MnO_2 cathode utilization and cathode porosity at 24 mA discharge rate.

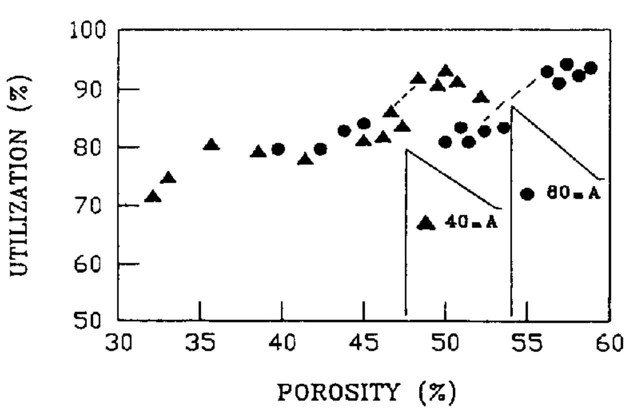

Fig. 2. Relationship between MnO_2 cathode utilization and cathode porosity at 40 and 80 mA discharge rates.

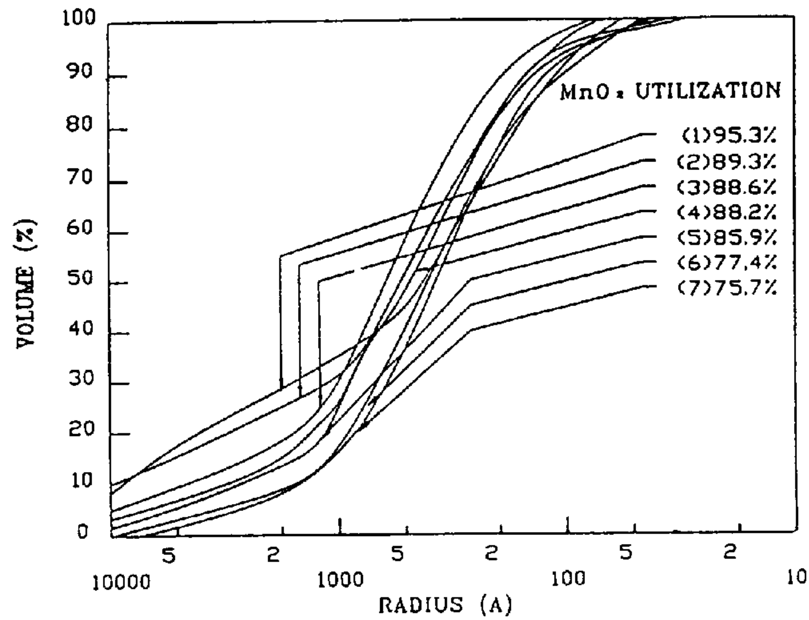

Fig. 3. Relationship between total volume percentage of the macropores and the pore-size distribution of the Li/MnO_2 cells with seven different cathode with the same constant porosity of ~48% utilization at 40 mA discharge rate.

increased from 80 to 90% as the electrode porosity increased from 45 to 48% for cell discharge at 40 mA. These results show that the electrode porosity must be higher than 42, 47, and 54% in obtaining more than 80% MnO_2 utilization at 24 mA, 40 mA, and 80 mA discharge current, respectively.

The effect of electrode pore-size distribution on MnO_2 electrode utilization of an 'AA'-size Li/MnO_2 cells at various pore diameters was examined (Fig. 3). The results show that the cathode utilization is sensitive to the cathode pore diameter and the total volume percentage of the 'macropores'. A high cathode utilization (>80%) can be obtained from a cathode with a total volume percentage of the macropores (diameter larger than 2000 Å) more than 25% of the total pore volume. These indicate that the 'macropores' of electrode are the dominant factor in determining the cathode utilization at high rate discharge. These suggest that the mass transport of the Li ion in the pore of the MnO_2 cathode contributes to the cathode performance at high rate discharge.

Conclusions

1. It was found that the higher porosity electrodes exhibit the higher utilization of Li/MnO_2 cells at high discharge rates.

2. The MnO_2 utilization of the Li/MnO_2 'AA' cells are strongly dependent on the pore-size distribution of the MnO_2 electrode.

3. MnO_2 electrodes with both high porosity and the large macropore volume percentage will be useful in the Li/MnO_2 cells at high rate applications.

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