Characteristics of a Li/MnO$_2$ battery using a lithium powder anode at high-rate discharge

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Abstract

The characteristics of lithium/manganese-dioxide cells using Li powder or Li foil as the negative electrode (anode) are compared at high-rate discharge. Lithium powders with a mean diameter of 20 μm are produced by forming a dispersion of molten Li metal in inorganic carrier fluids. Cells using Li powder anodes show larger capacity and lower internal resistance than cells using Li foil anodes. Based on BET (Brunauer–Emmett–Teller) measurements, a reduction of effective current density due to the large surface area of the Li powder is considered to be responsible for the superior higher-rate discharge characteristics.
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1. Introduction

For the past two decades, there has been enormous international activity in the development of lithium batteries, both primary and secondary. The interest stems from the fact that lithium has a low atomic mass (6.94 amu), a high specific capacity (3.86 Ah/g) and a high electrochemical reduction potential (−3.04 V); all of which contribute to a high specific energy for Li cells [1].

The primary Li/MnO$_2$ cell was one of the first Li cells to be commercialized. In general, Li/MnO$_2$ cells were designed for low-current discharge applications, due to considerations of safety and rate capability. Since then, there has been an increasing demand for batteries with high power and high specific energy for use in many applications such as portable computers, portable power tools, and industrial and medical instruments. Li/MnO$_2$ cells have become promising candidates for such applications [2]. There is, however a severe capacity loss in these systems under high-rate discharge.

Many workers have studied Li powder negative electrodes (anodes) as a means to improve the performance of Li cells. Using compacted Li powders, dendritic growth of lithium has been restricted remarkably during the charge–discharge process [3]. A Li polymer cell with such an anode has been shown to give a somewhat larger cycle-life and higher discharge capacity at low temperatures [4]. Also, in the Li/SOCl$_2$ primary system, the voltage-delay phenomenon at high pulse discharges has been suppressed when using a Li powder anode [5]. From these results, it has been concluded that the surface film formed on a Li powder anode is more stable than that on Li foil, due to its sound, uniform and low resistive nature [6].

In this paper, a Li powder anode has been developed for the Li/MnO$_2$ system. Coin-type, primary Li/MnO$_2$ cells using this electrode have been evaluated under high-rate discharge.

2. Experimental

2.1. Preparation of lithium powder

Lithium powders were produced by a droplet emulsion technique (DET) [3]. A mixture of molten Li and an inorganic carrier fluid was sheared at around 20 000 rpm to produce an emulsion. As the emulsion cooled down to room temperature, the Li droplets became solidified. Lithium powder was then separated from the oil and cleaned with hexane. Details of the DET have been presented elsewhere [3,7,8]. The powders made in this study had a mean diameter of around 20 μm.

[*] Corresponding author. Tel.: +82-2-3290-3274; fax: +82-2-928-3584.
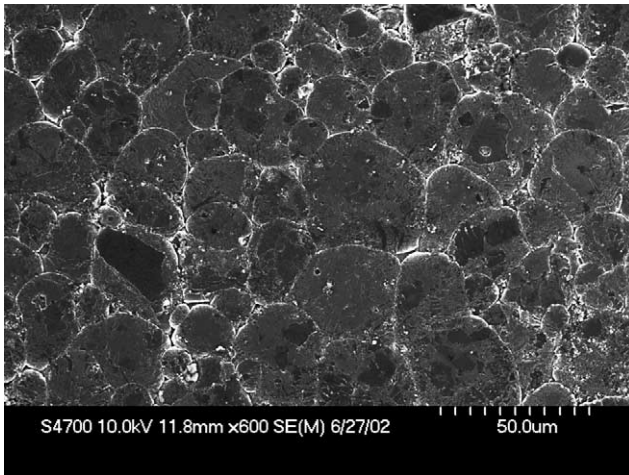*E-mail address:* wyyoon@korea.ac.kr (W.Y. Yoon).

Fig. 1. Typical microstructure of compacted Li powders.

To evaluate electrochemical performance, the Li powders were compacted to a coin shape (15 mm diameter, 0.7 mm thickness) by applying a pressure of around 15 MPa. The typical microstructure of the compacted Li powders is shown in Fig. 1.

2.2. Coin-type cell test

Discharge characteristics and impedance analysis of the Li/ MnO_2 system were examined using coin-type cells. The configuration of the standard coin cell (CR2032: diameter 20 mm, height 3.2 mm) used in the experiments is shown in Fig. 2. Compacted Li powder and Li foil with the same dimensions (i.e. geometric surface area of 1.77 cm^2), were used as negative electrodes. The Li foil was obtained from the
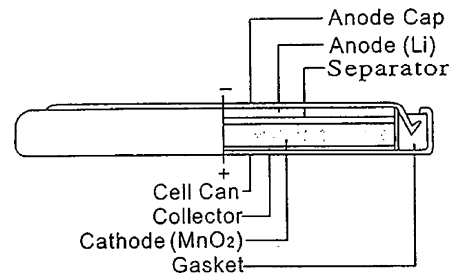

Fig. 2. Schematic diagram of standard coin-type cell (CR2032).

Cyprus Co., USA (with a purity 99.9%), whilst the Li powders were manufactured and compacted in the laboratory. The electrolyte used was 0.75 M $LiCF_3SO_3$ in 1:2 by volume ratio of propylene carbonate (PC) and 1,2-dimethoxyethane (DME). The positive electrode (cathode) was obtained from Shun Wo New Power Electronics Ltd. (Hong Kong, China) as commercial coin-type manganese dioxide. Cell preparation (including powder making and assembly) was carried out in a glove box under an argon atmosphere.

After assembly, some cells were stored at room temperature for 20 days whilst others were stored at 60 °C for 20 days. Discharge experiments were conducted with a constant current of 2 mA (1.13 mA/cm^2) and a cut-off voltage of 3.0 V. Pulse-discharge tests used successive pulses with 0.45 mA (0.25 mA/cm^2) and 10 min as a standby current and 20 mA (11.3 mA/cm^2) and 1 s as a run current.

2.3. BET measurements

In order to understand any differences in the discharge characteristics between Li powder cells and Li foil cells, it is
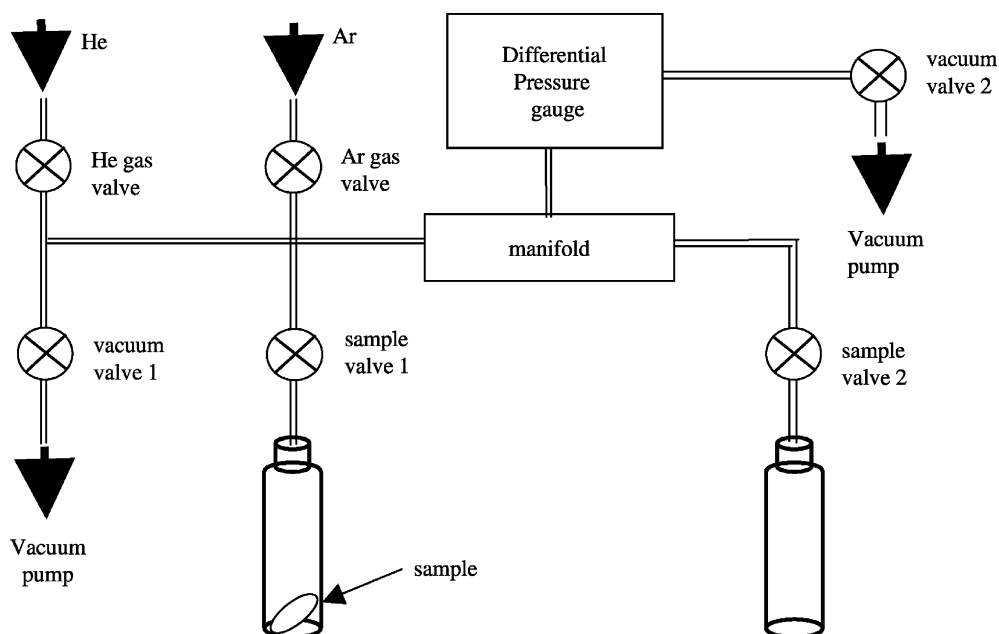

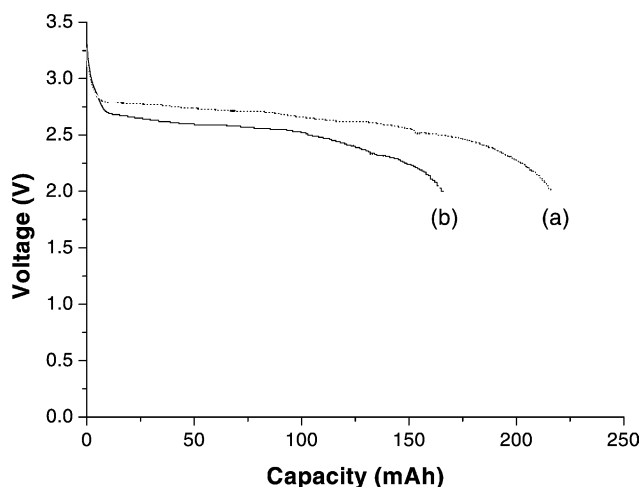Fig. 3. Schematic diagram of specific surface-area measurement system [9].

Fig. 4. Typical discharge characteristics of Li foil and Li powder cell at 2 mA constant-current discharge after 20 days storage at room temperature: (a) Li powder anode cell; (b) Li foil anode cell.

important to measure the effective surface area of both types of anode. The specific surface area was measured with an ASAP 2010 instrument (Micromeritics Co., USA) with the setup shown schematically in Fig. 3 [9].

The BET (Brunauer–Emmett–Teller) method is generally used to measure surface area by calculating the amount of gas adsorbed in a specimen. To measure the effective surface area of Li powder and Li foil anodes successfully, the following experimental conditions have to be optimized. First, argon (purity 99.9999%) was used as the adsorption gas because it does not react with lithium. By contrast, nitrogen, is generally used as the adsorption gas for this measurement due to its high adsorption power and low cost, reacts with lithium to form Li_3N [9,10].

2.4. Impedance measurements

The electrochemical behaviour of cells which used Li powder or Li foil anodes was analyzed by impedance measurements (IM6, Zahner, Germany). These were performed at open-circuit potential in accordance with the storage time. The amplitude of the applied alternating potential was ±5 mV and its frequency was varied from 100 kHz to 100 mHz. All measurements were performed at room temperature.

3. Results and discussion

3.1. Discharge and pulse characteristics of cells

The typical discharge characteristics of two cells after 20 days of storage at room temperature are shown in Fig. 4. The discharge current (2 mA) is considered to be a condition of high-rate discharge since the standard current of this model (CR2032) is about 0.2 mA [11–14]. There is considerable improvement in terms of discharge performance when using a Li powder cell (216 mAh) compared with a Li foil cell (164 mAh).

The typical discharge characteristics of two cells with Li powder and Li foil anodes after 20 days of storage at 60 °C are given in Fig. 5. The test condition is known to be the equivalent of about 1 year's storage at room temperature. Again, the Li powder cell yield higher capacity (207 mAh) than the Li foil cell (164 mAh).

The capacity of the Li/MnO_2 system is considered to be strongly dependent to the conductivity of the electrolyte solution [15], the operating temperature [16], and the pore size and distribution of the cathode [17]. Furthermore, the
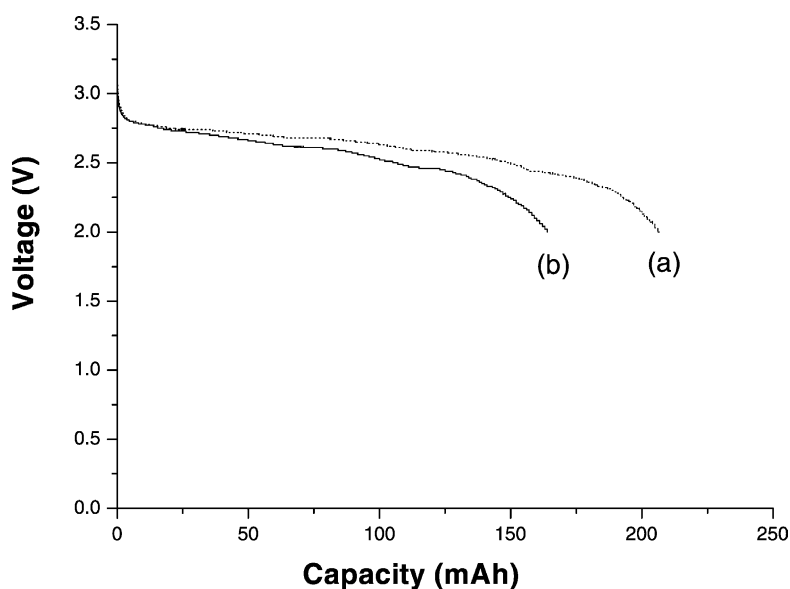

Fig. 5. Typical discharge characteristics of Li foil and Li powder cell at 2 mA constant-current discharge after 20 days storage at 60 °C: (a) Li powder anode cell; (b) Li foil anode cell.
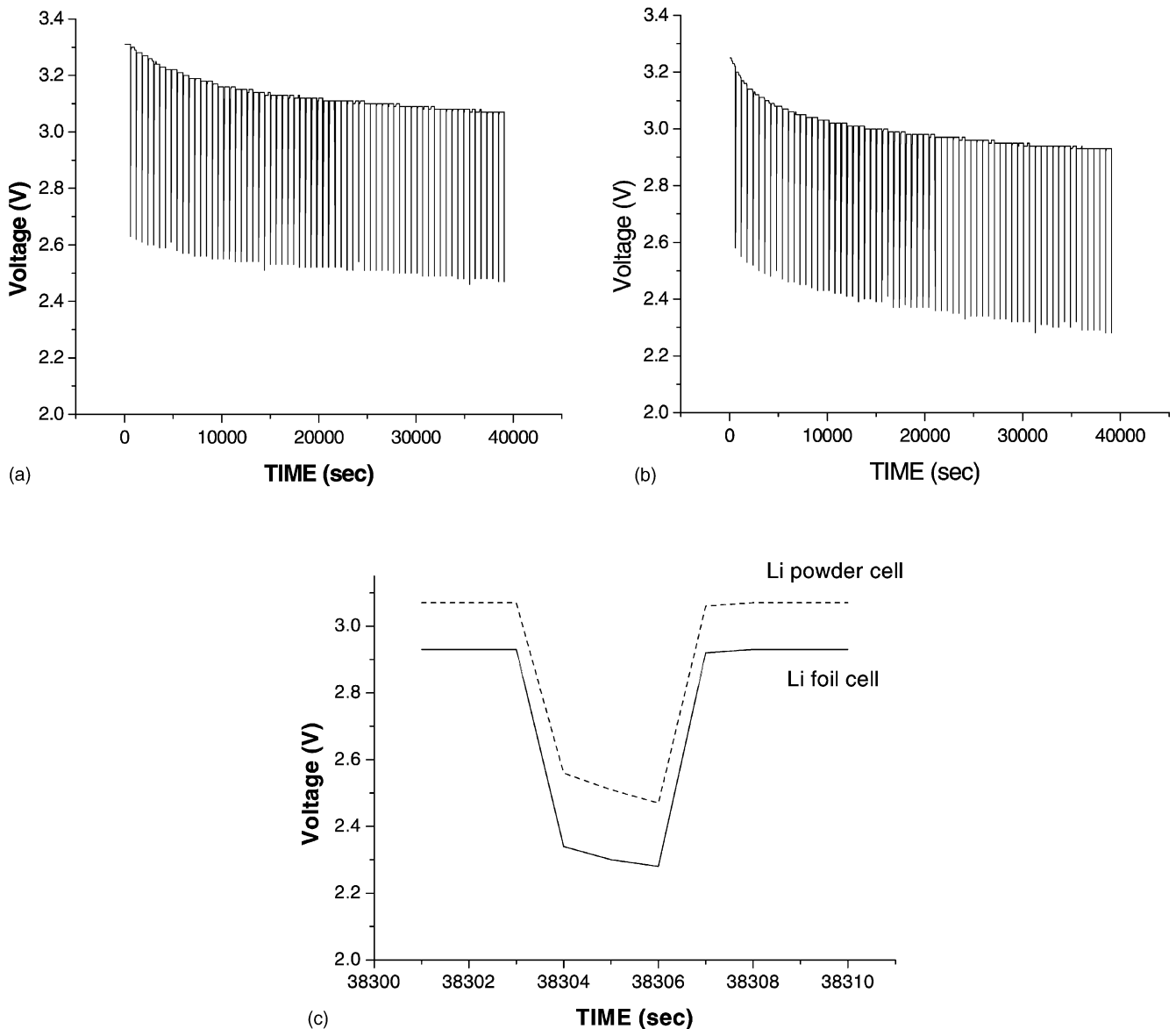
Fig. 6. Pulse-discharge characteristics of two cells after 20 days storage at 60 °C (stand-by current = 0.4 mA, 10 min; run current = 20 mA, 1 s: (a) Li powder anode cell; (b) Li foil anode cell; (c) voltage behaviour of two cells at 65th (final) pulse.

discharge capacity at high rate is related directly to the current density, and thus to the total active electrode surface area of the cells [18]. Therefore, it seems that the improvements made in the discharge performance of Li powder cells is related to the variation of current density, which results from the difference in the reactive surface area between this anode and the Li foil anode (see below).

The pulse-discharge characteristics of two cells after 20 days storage at 60 °C are shown in Fig. 6. The voltage behaviour of two cells on the 65th pulse (the final one) are given in Fig. 6(c). The Li powder cell has not only stable and superior pulse characteristics, but also a higher transient minimum voltage. To analyze these results more accurately, the following BET measurements were performed.
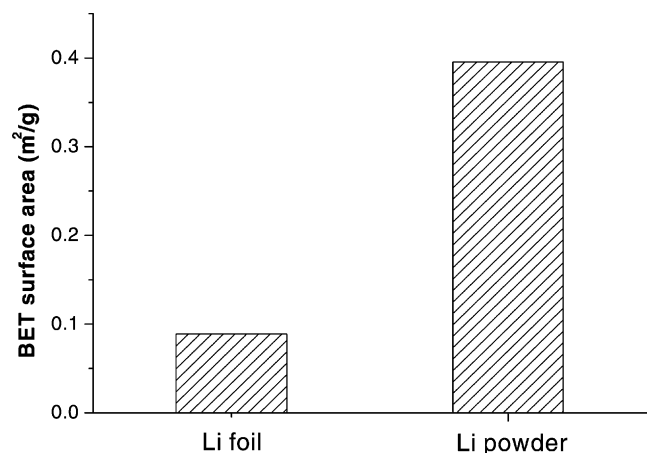

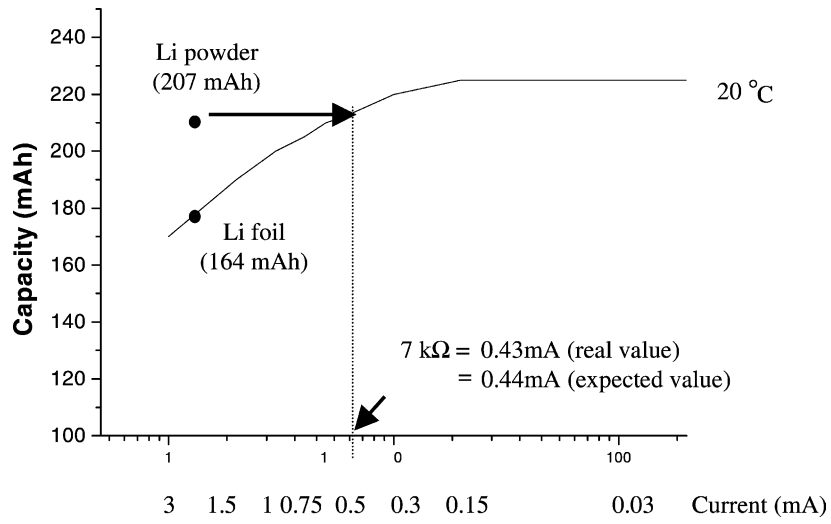Fig. 7. BET specific surface area of Li foil and Li powder anodes.

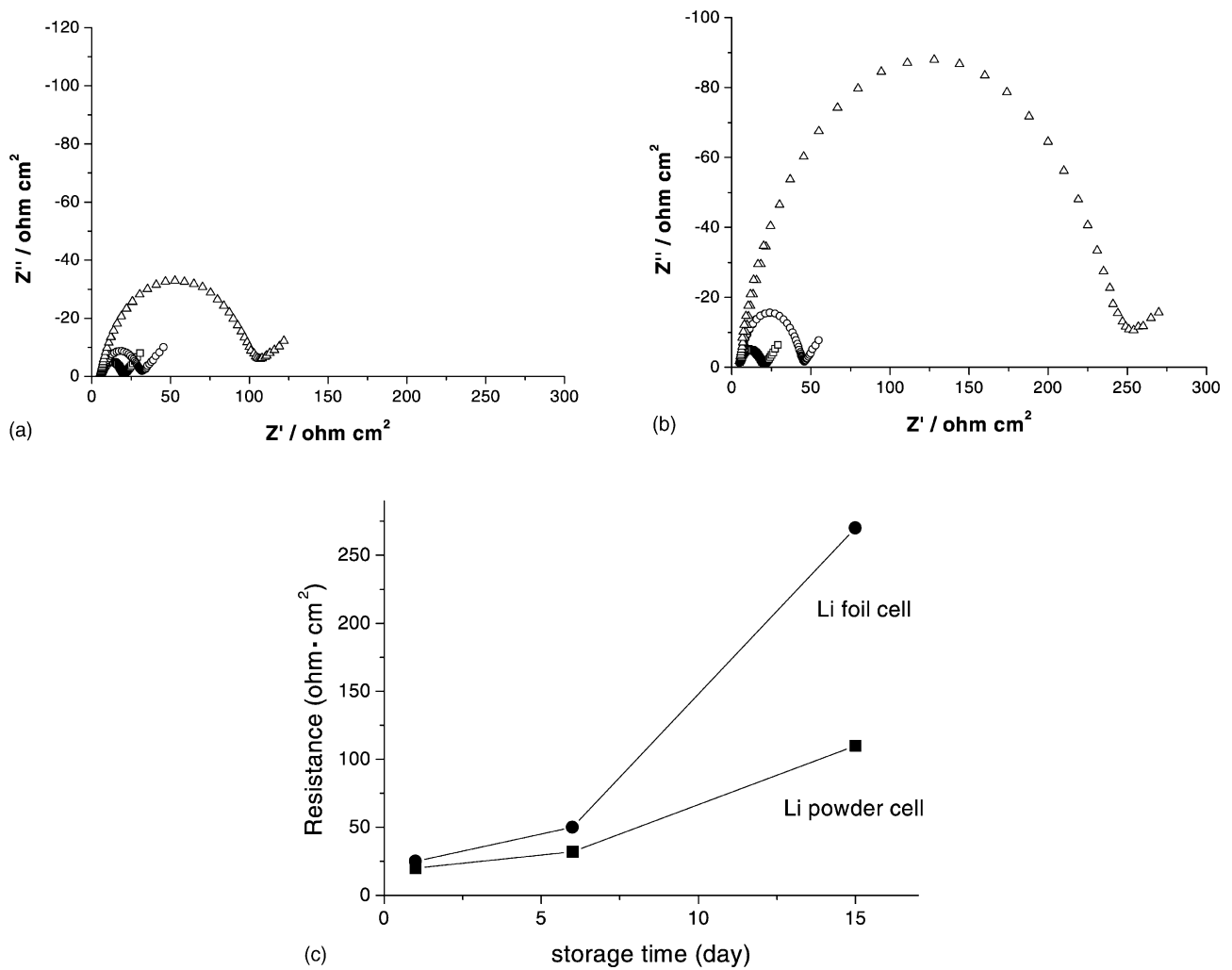Fig. 8. Load or current–capacity relation in Li/MnO$_2$ battery (CR2032).

Fig. 9. Impedance measurements of two cells stored at 60 °C with storage time: (a) Li powder anode cell; (b) Li foil anode cell (after: (□) 1 day, (●) 6 days, (△) 15 days); (c) resistance of two cells.

3.2. BET measurements of Li powder and Li foil anodes

The BET specific surface areas of the Li powder and Li foil anodes are shown in Fig. 7. Although the two anodes have the same geometrical surface area (1.77 cm^2), it is evident that the effective reactive surface area of the Li powder anode (0.40 m^2/g) is much larger than that of the Li foil (0.089 m^2/g) by counterpart.

Generally speaking, when a constant current flows across the surface of the electrode, the effective current density (current density per reactive surface) decreases as the surface area increases. If the surface area of the Li foil anode is 'A' and the constant discharge current is 'I', then the current density across this anode will be 'I/A'. In the case of the Li powder anode, however the effective current density is $I/4.5A$ due to its greater surface area under the present experimental conditions. Therefore, the higher surface area of the Li powder anode probably lowers the discharge current density ($I/4.5A = 2$ mA/4.5 $= 0.44$ mA), and thereby enhances its discharge capacity.

In an attempt to verify the above assumption, the dependence of discharge capacity on current is presented in Fig. 8 [11–14] for a commercial Li/MnO$_2$ cell (CR2032, Shun Wo New Power Electronics, Hong Kong, China) [12]. According to this relationship, the capacity of the commercial cell (about 165 mAh) is in good agreement with the capacity of Li foil cells (164 mAh) at constant-current discharge of 2 mA. This relationship cannot, however be explained by the higher capacity of Li powder cells (207 mAh), even if a 1-year equivalent storage is assumed. The higher capacity (207 mA) value requires a discharge current of less than 0.43 mA or an external load of more than 7 kΩ (see Fig. 8). It is similar to the value of the 0.44 mA discharge current predicted above. Hence, it can be concluded that the reason for higher capacity in Li powder cells is the decrease in effective current density on the anode due to an increased reactive surface area.

3.3. Impedance measurements of Li powder and Li foil cells

The impedance of Li powder and Li foil cells stored at 60 °C as a function of storage time is shown in Fig. 9. The values of the resistance of the surface film on Li anodes were obtained from the diameter of the semi-circle [5,19,20]. The resistance of the Li powder anode varies from 13 to 100 Ω whilst in this storage condition. By contrast, the resistance of the Li foil anode varies from 17 to 250 Ω. The surface-film resistance of the Li foil anode is larger than that of a Li powder anode, with the latter increasing slowly and the former increasing continuously with storage time (Fig. 9(c)). The lower resistance of the surface film on the Li powder anode agrees with other reports [3–5].

Because lithium metal is thermodynamically unstable with regard to the electrolytes of Li batteries [11], further reaction between the two materials occurs continuously. As a result, the surface film resistance of the Li anode increases with storage time. The impedance results therefore indicate that the surface film of Li powder anodes prevent further reaction, compared with Li foil anodes.

Despite these observations, the above characteristics do not appear to be a major determinant of high-rate discharge performance as it can be observed that the current magnitude of an initial few μA can easily break the surface films on the Li anodes in this system. This is mostly attributed to the available surface film on the Li anodes and its structure within the system [11,21–26].

The characteristics of surface film on Li powder anodes may be very important in other systems in controlling the electrochemical properties, e.g. Li/SOCl$_2$ primary batteries, Li metal secondary batteries and Li polymer batteries, etc. [3–6].

4. Conclusions

Lithium metal powder has been prepared as a negative electrode for a Li/MnO$_2$ primary system. The compacted lithium powder cell yields larger capacity and appears to have more stable pulse characteristics than lithium foil cells. It is suggested that the higher reaction area of Li powder anodes probably lowers the effective discharge current density on anodes, and thus enhances the high-rate discharge characteristics. Moreover, a lower resistance of the surface film on Li powder anodes is expected to produce an excellent electrochemical performance from these anodes in other systems.

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