

Battery dimensional changes occurring during charge/discharge cycles—thin rectangular lithium ion and polymer cells

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Abstract

During cycles, the battery thickness changes for the three reasons—(i) expansion and contraction of host materials due to lithium intercalation, (ii) electrode volume increase caused by irreversible reaction deposits, and (iii) dead volume and pressure changes within the cell case depending on battery structure and construction. In this study we have identified and quantified those three reasons and related thickness increases employing commercially available thin prismatic lithium ion and polymer cells.

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1. Introduction

Quite contrary to the common perception that battery thickness remains constant during everyday use, the lithium ion and polymer batteries are structurally and dimensionally dynamic. The batteries generally expand during charge and contract during discharge. This thickness, thus volume, change is caused by lithium ion intercalation into host materials, i.e. graphite and lithium transition metal oxide and resultant lattice expansion and contraction [1–5]. Expansion of carbon materials are observed to be much more significant than lithium cobalt oxide (LiCoO₂) [3]. For carbons, the degree of expansion greatly varies depending on the structure. For example, natural graphite shows almost three times greater volume change than MCMB [6,8]. Quantitatively about 10% increase in lattice parameters was observed by X-ray diffraction [1].

While reversible is the volume change within crystal lattice spacing of carbon materials, the thickness increase occurs with cycles is irreversible. The irreversible increase may be attributed to the electrode reactions with electrolytes that tend to have insoluble deposits accumulated on the electrode surface. For some graphite anode materials, larger volume expansion is noted to result from the irreversible reactions than that caused by the lithium intercalation reaction [7].

Aside from the two reasons for the thickness growth mentioned above, we also have found that the battery design

and construction affect significantly the thickness change. This study summarizes results from several different types of cells—lithium ion and polymer cells, stacked and strip-wound designs, and soft pouch and hard metal enclosures. Most surprisingly, polymer cells with soft packaging exhibited the least amount of thickness increase during charge and cycles. Regarding battery structure, stacked-design shows lesser expansion than strip-wound design (the so-called “jelly roll”).

2. Experimental

The batteries employed in this study were 383562 polymer cells from LG [9–11] and others, similar size pouch lithium ion cells from another manufacturer, and rectangular-can lithium ion cells from yet another source. Table 1 summarizes the sources and characteristics of the cells tested in this study. The detailed chemistry and structure of LG's polymer batteries were disclosed elsewhere [9–11].

The thickness measurement was performed in situ using a thickness gauge equipped with constant load and connected to an automatic data logger. As is shown in Fig. 1, a sample battery was placed between two parallel plates. The upper plate carries a constant load, approximately 300 g in this study and is connected to a low-friction guide. Electric cables were attached to the sandwiched battery for charge and discharge. The measurement system and battery was placed in a thermostat chamber during cycles (Fig. 2).

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Table 1
Batteries tested in this study

Manufacturer	Type	Structure	Enclosure	Battery size ($T \times W \times L$) (mm)	Capacity (mAh)
LG	Polymer cell	Stacked	Soft package	$3.8 \times 35 \times 62$	780
Manufacturer A	Polymer cell	Wound	Soft package	$3.8 \times 35 \times 62$	720
Manufacturer B	Lithium ion cell	Wound	Soft package	$3.8 \times 35 \times 62$	670
Manufacturer C	Lithium ion cell	Wound	Metal can	$3.8 \times 34 \times 50$	550

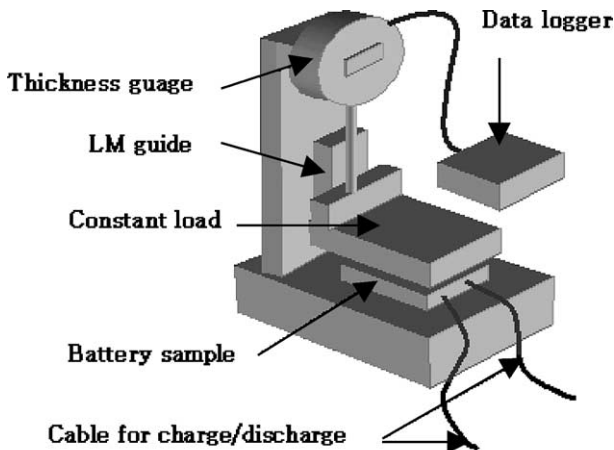


Fig. 1. Schematic illustration of thickness monitoring equipment.

Battery charging was done at constant-current (typically 1 C rate) and with constant-voltage limit of 4.2 V. Charging was terminated with an end current of approximately 0.05 C rate. Discharge was at constant 1 C current with end voltage of 3.0 V. The rest time was about 20 min between each charge and discharge mode. All measurements were done at room temperature.

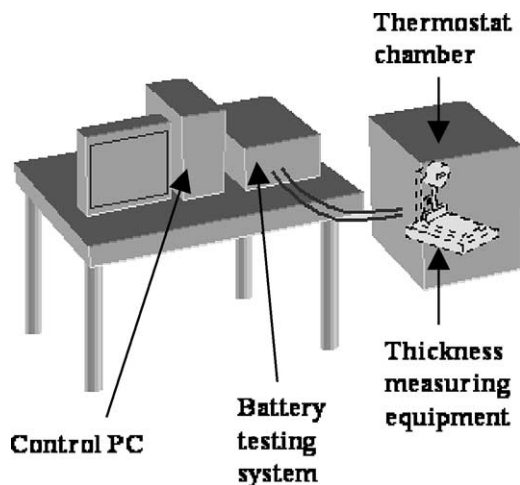


Fig. 2. Schematic illustration of in situ measuring system during charge and discharge.

3. Results and discussion

3.1. Irreversible thickness increase during first charge

First of all, irreversible increase in battery thickness was observed during the first charge, the so-called “formation.” As seen in Fig. 3, the thickness growth is rather steep when the cell voltage rises from zero to about 2.8 V. In this voltage range electrolyte reduction takes place on the carbon anode to form a SEI layer on the exterior of carbon surface [1,2,12]. It appears that the electrolyte reduction on the anode surface causes a rapid volume increase [7,12]. The reaction products deposited on the exterior of carbon material seem to cause the volume increase in the anode. This first charge resulted about a 4% increase in the battery thickness. Almost half of this 4% increase occurred in the initial part where only about 10% of total charge was passed (SOC = 10%).

3.2. Reversible thickness fluctuation upon charge/discharge cycling

After the formation cycle, thickness change is mainly caused by expansion and contraction of host materials. Typical periodic expansion and contraction cycles were noted for all the cells as in Fig. 4. The cycles coincide well with the voltage profiles. As was expected, the battery expands when charged and vice versa. The difference between peak and bottom is about 0.06–0.07 mm for 383562 polymer cells. That corresponds to about 2% of total thickness. Generally, it is reported that graphite anode materials have about 10% of volume expansion during charge [1]. If we accept about half of 10% is due to SEI deposits as discussed above, the remaining 5% can be translated into about 2% increase (the anode volume occupies about 35% of total battery volume), which corresponds well with the experimental observation. All of these observations seem to indicate the thickness variation is mainly attributed to anodic volume change.

3.3. Influence of battery internal structure on the amplitude of thickness swing

Fig. 5 presents the results from soft-packaged lithium ion cell from Manufacturer B. Compared to the results from LG’s polymer cells, this cell has larger variation with the maximum displacement being about 0.12–0.14 mm for this

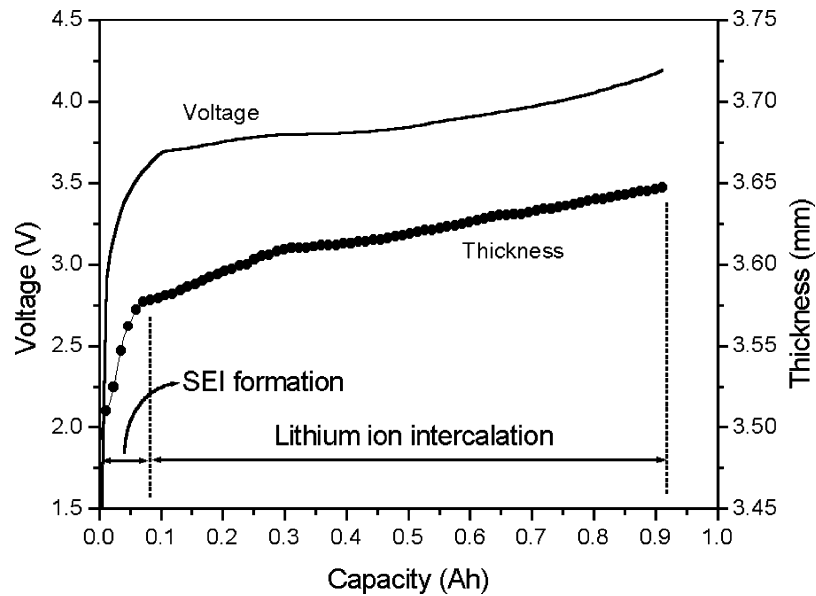


Fig. 3. Increase of battery thickness during first charge at 0.05 C rate from LG’s polymer cell, size 383562.

type cell. That corresponds to about 4% of total thickness and twice to that of LG’s polymer cell. We may speculate two reasons for the observed difference. First, the carbon anode materials adopted by the Manufacturer B may have larger volume changes. Indeed, some flaky graphites do show significantly larger volume expansion upon lithiation [6]. Second, battery structure may have brought the larger increase. The Manufacturer B’s cells have plain wound structure. And the wound structure is prone to distortion during cycles [13]. Since LG cell is constructed via stack and fold method [9–11], the stress causing distortion is fully relaxed.

It was noted that for the LG cell in Fig. 4, the thickness begins to decrease slightly when the cell voltage reaches the

charge limit. This observation is not well understood at this moment but can only be speculated as follows. As seen in Fig. 4, at this high-rate charge, we may expect lithium ion intercalation/deintercalation may not be uniform as state of charge reaches maximum and the electrode volume changes may overshoot. But after reaching constant-voltage with the charge current quickly decreased the nonuniformity tends to disappear, thereby relaxing the stress. Another probable explanation could be the structural difference. Since the LG cell is stack-and-folded, the quickly-developed stress caused by the expansion of the electrodes can be relaxed without causing distortion, while the wound structure cannot help deforming.

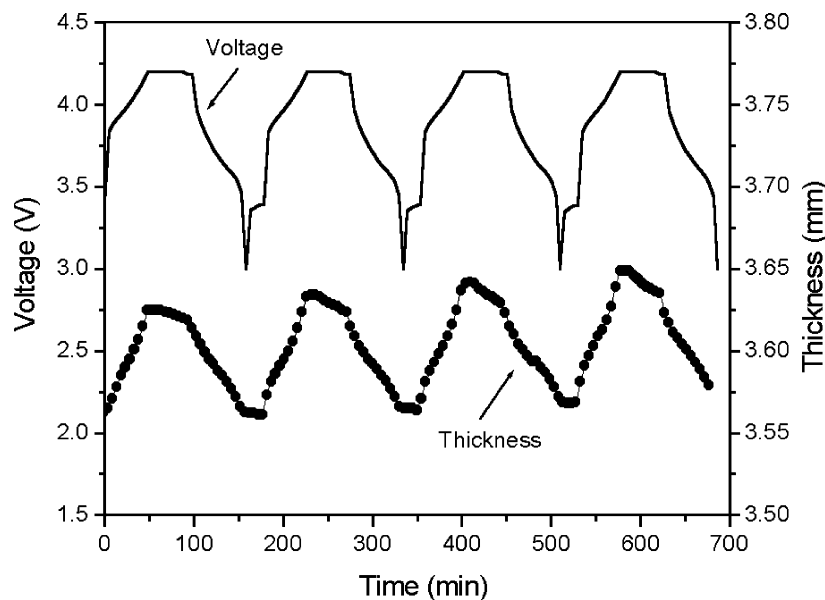


Fig. 4. In situ measurements of battery thickness during charge/discharge cycles at room temperature. The battery is LG’s polymer cell, size 383562.

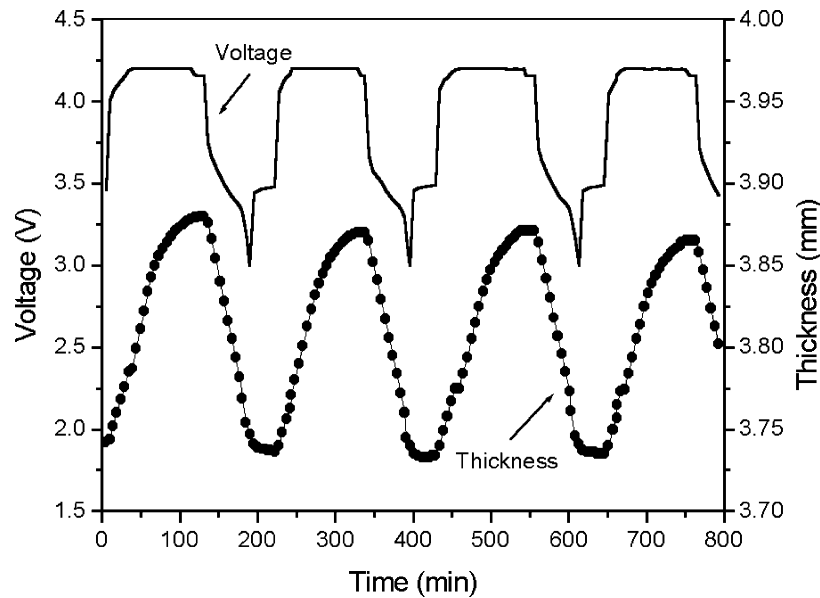


Fig. 5. In situ measurements of battery thickness during charge/discharge cycles. Battery from Manufacturer B. Pouch packaged lithium ion cell, size 383562.

3.4. Battery enclosure effects

Comparisons between manufacturers and different types of cells were made in Fig. 6. Prismatic lithium ion cells (type 383450) encased in aluminum cans noticeably exhibit the largest increase in thickness with the thickness amplitude being almost 0.2 mm, which is about three-fold of LG's polymer cells. In general we do see most of the jelly rolls are prone to twisting and deformation upon the stress built up by the volume change of lithium-intercalated carbon materials [1,2]. This effect appears to be aggravated further in metal cases while soft pouch can effectively absorb the

dimensional stress especially when the packaging is carried out under degassed conditions. Contrary to common perception, prismatic metal can batteries (lithium ion) actually have larger thickness fluctuations than well-prepared pouch cells. It may be a little difficult to understand why but it is now a ubiquitous phenomenon in this industry. Battery pack producers actually give larger margins when metal can batteries are used. This larger thickness change is mainly due to the gas pressure inside the can. The gaseous products are generated during the first charge, "formation". The internal pressure of prismatic can batteries is almost always higher than the atmospheric. Therefore during charge when

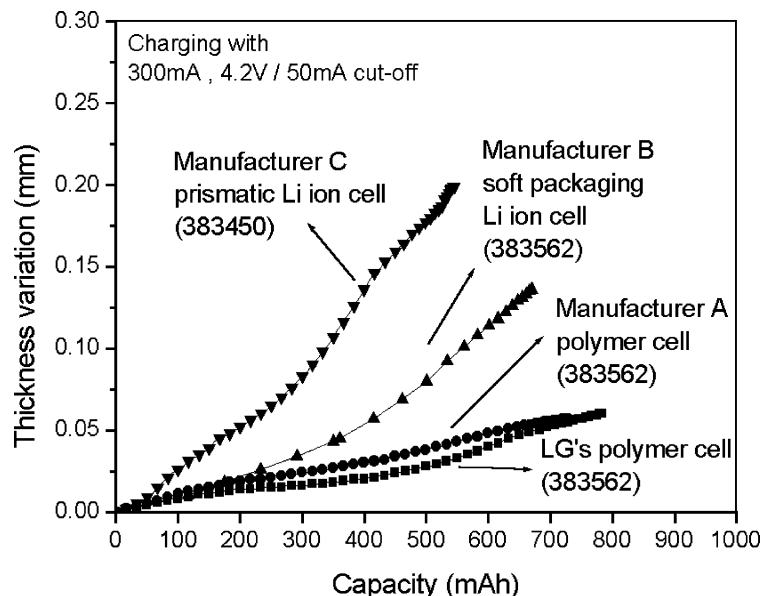


Fig. 6. Influence of different battery construction on thickness increase.

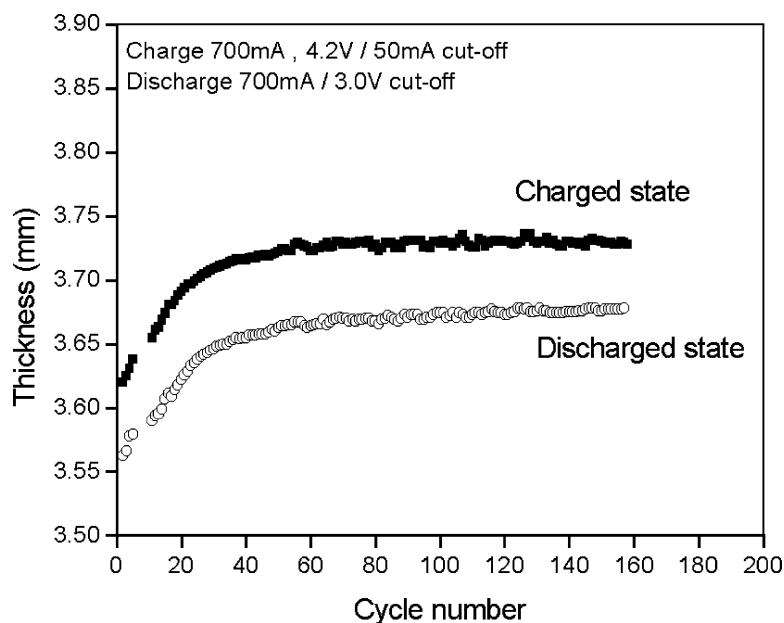


Fig. 7. Variation of thickness during long cycles. The battery is LG's polymer cell, size 383562.

electrodes expands, the overall cell thickness is more or less amplified. Meanwhile when the pouch is used instead as an enclosure, the cells are usually degassed and resealed after the first charge. Therefore the internal pressure is always negative.

3.5. Battery thickness increase during prolonged cycles

During prolonged battery cycles, the overall battery thickness grows gradually for the first 40 cycles, and after reaching maximum after 70 cycles, almost no further increase was observed (Fig. 7). During first 40 cycles, the polymeric compounds such as binder, gel polymer and separator may have been swollen with electrolyte. The battery has its maximum thickness when fully charged, and minimum thickness when fully discharged. The maximum displacement between fully charged and fully discharged did not change much as the cycle number increased.

4. Conclusions

We have investigated the thickness changes occurring during charge/discharge cycles for flat prismatic lithium ion and polymer batteries. An irrecoverable thickness increase of at least 4% of initial thickness was observed during the first charge. After the first cycle, the thickness fluctuates reversibly with peaks reached at full charge. The amplitude of the fluctuation seems to be dictated by the type of carbon anode materials and battery structure. The total thickness increase amounts to at least 6% of the initial

thickness. Comparisons with various manufacturers showed LG's polymer cells posted the least amount of thickness change. Regarding battery enclosure, most surprisingly pouch cells gave much smaller thickness change than the metal case cells. This volume expansion phenomenon must be taken into account for power pack designs, modeling studies, and especially for the designs of larger modules where numerous individual cells are stacked and connected.

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