Effect of Formation Potentials on Gassing of
LiMn$_2$O$_4$//Li$_4$Ti$_5$O$_12$/C Batteries

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Spinel Li$_4$Ti$_5$O$_12$ has been considered as a promising alternative material to graphite for lithium ion batteries (LIBs) with improved safety and cycle life. Unfortunately, the destructive gas generation of Li$_4$Ti$_5$O$_12$ and the associated cell swelling have been a major obstacle to the large-scale application of LIBs using Li$_4$Ti$_5$O$_12$-based anodes. In this paper, we investigate the surface evolution of the anode in LiMn$_2$O$_4$/Li$_4$Ti$_5$O$_12$/C cells and the role of formation potential on the gassing of LiMn$_2$O$_4$/Li$_4$Ti$_5$O$_12$/C cells. It was found that an appropriate high potential formation protocol for LiMn$_2$O$_4$/Li$_4$Ti$_5$O$_12$/C batteries can effectively inhibit the gassing and enhance the cycling performance of these LIBs. This is mainly because under high formation protocol, an artificial flexible solid-electrolyte interphase film can be formed on the surface of Li$_4$Ti$_5$O$_12$/C, which further prevents electrolyte decomposition at the electrolyte/Li$_4$Ti$_5$O$_12$/C interface.

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Figure 1. (a) First charge/discharge curves of LMO cathode, (b) first charge/discharge curves of LTO/C anode, (c) initial charge/discharge curves of LMO/LTO/C batteries with 3.0 V upper potential, (d) initial charge/discharge curves of LMO/LTO/C batteries with 3.2 V upper potential, (e) thickness variation of LMO/LTO/C pouch batteries with different upper potentials, and (f) cycling performance comparison of LMO/LTO/C batteries with different formation potentials.

LM011, Hunan Shanshan Advanced Materials Co. Ltd., Changsha, China) cathode materials. LTO/C anode was synthesized according to a previous report by a solid-state reaction method. For assembly in full batteries, the LMO electrode consisted of 94 wt% LMO, 3 wt% conductive carbon black, and 3 wt% polyvinylidene difluoride (PVDF) (HSV 900, Solvay, Belgium). The LTO/C electrode consisted of 92 wt% active materials, 3 wt% conductive carbon black, and 5 wt% PVDF as a binder. After being mixed thoroughly, the LMO and LTO/C slurries were coated onto aluminum and copper foil separately, with a subsequent calendering. The calendered densities of the LMO and LTO/C electrode are 2.8 g/cm³ and 1.7 g/cm³, respectively. In this experiment, to design the coating density, LMO and LTO/C were first characterized in CR2025 coin cells, using Li metal as the negative electrode and 1 M LiPF₆ in a 1:1:1 mixture of ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC) was used as the electrolyte (Shenzhen Capchem Technology Co., Ltd., China). To improve the cycle performance and prevent LMO cathode from overcharging, the designed LMO/LTO/C cell capacity is determined by LTO anode, and the capacity ratio of LMO/LTO/C is about 1.10.

To assemble LMO/LTO cells, 1 M LiPF₆ in a 1:1:1 mixture of EC/DMC/DEC was used as the electrolyte (Shenzhen Capchem Technology Co., Ltd., China), and Celgard 2500 was used as the separator. The cathode, anode, and separator were stacked together to make the cell core, and then the core was put into aluminum plastic-laminated film pouches. The electrolyte was injected, and the batteries were sealed with a sealing machine. The cell assembly was conducted in an argon-filled MBraun glove box.

Characterization.—The formation and cycling tests of full cells were all performed using a LAND 2001A cell testing system (Wuhan Land, China) at room temperature. Two protocols were used to evaluate the effects of formation potentials, as shown in Fig. S1 in the supporting information. The high potential formation protocol (Fig. S1a) is as follows: (1) galvanostatic charge at 0.1 C until the potential reaches 3.2 V; (2) galvanostatic discharge at 0.1 C until the potential reaches 1.5 V; (3) after the first three formation cycles, galvanostatic charge at 1 C until the potential reaches 3.2 V; (4) potentiostatic charge at 3.0 V until the current is less than 0.1 C; and (5) galvanostatic...
discharge at 1 C until potential reaches 1.5 V. On the other hand, the low potential formation protocol is as follows: (1) galvanostatic charge at 0.1 C until the potential reaches 3.0 V and (2) galvanostatic discharge at 0.1 C until potential reaches 1.5 V. After the first three formation cycles, steps (3), (4), and (5) are identical to those in the low potential formation protocol (Fig. S1b). Fig. S2 shows the procedure for measuring the thickness of the LIBs after cycling.

To investigate the surface composition of the electrodes, full cells were disassembled in a high-purity Ar atmosphere at different formation potentials with respect to the discharged state, rinsed thoroughly with dimethyl carbonate (DMC) solution and transferred to the Fourier transform infrared spectroscopy (FTIR, Nicolet IS 5) and X-Ray photoelectron spectroscopy (XPS) apparatus. XPS was conducted on an ESCALAB 250 spectrometer using an Al Kα radiation.

Results

Figs. 1a and 1b show the first charge/discharge profile of the LMO cathode and LTO/C anode, which have specific capacities of 110 and 165 mAh/g, respectively. The effect of the upper potential formation on the electrochemical performance and gassing of the LMO/LTO/C system was then evaluated from pouch cells containing these electrode materials. Figs. 1c and 1d shows the first formation curves of the cells with different upper potentials at 0.1 C. Obviously, the cell obtained at the high upper formation potential (3.2 V) showed a significantly lower initial coulombic efficiency (94.3%, Fig. 1d) than that obtained at the normal formation potential (3.0 V, 96.0%, Fig. 1c). With the increasing cycles, the cells obtained at the ordinary formation potential, however, showed an apparent gassing and swelling. Fig. 1e shows the changes in the thickness of the two types of LMO/LTO/C cells during cycling. It can be seen that the ordinarily formatted cells show about a 60% increase in thickness after 100 cycles, while the ones formatted at the high potential only show about a 10% thickness increase or swelling. Moreover, the high-potential formatted cells also showed better cycling performance than those formatted at the ordinary potential (Fig. 1f). The capacity retention of the batteries formatted at 3.2 V is about 94.2% after 200 cycles. In contrast, the capacity retention of those formatted at 3.0 V batteries is only ~79% after 200 cycles. This clearly indicates that the high-potential formation protocol not only effectively suppresses gassing, but also significantly improves the electrochemical performance.

The surface compositions of the LTO/C electrodes after formatting at different formation potentials were then characterized by FTIR spectroscopy. Fig. 2 shows the FTIR curves of PVDF binder and the LTO/C electrodes formatted at 2.8, 3.0 and 3.2 V in the LMO/LTO/C cells. It can be found that the bands for (CH2OCO2Li)2 and Li2CO3 at different formation potentials were then characterized by FTIR the electrochemical performance. This clearly indicates that the high-potential formation protocol not better cycling performance than those formatted at the ordinary potential only show about a 10% thickness increase or swelling. Moreover, the high-potential formatted cells also showed better cycling performance than those formatted at the ordinary potential (Fig. 1f). The capacity retention of the batteries formatted at 3.2 V is about 94.2% after 200 cycles. In contrast, the capacity retention of those formatted at 3.0 V batteries is only ~79% after 200 cycles. This clearly indicates that the high-potential formation protocol not only effectively suppresses gassing, but also significantly improves the electrochemical performance.

In summary, the FTIR, XPS, and electrochemical performance results all prove that a different electrochemical interface reaction might occur at the high formation potential of 3.2 V, which can be linked to less gassing and the superior cycling performance of LMO/LTO/C batteries, as shown in Fig. 1.

Discussion

During the initial formation process for graphite-based LIBs, gas generation is one of the major issues, as a result of electrolyte decomposition and SEI formation. Typically, the generated gasses are evacuated after formation during the battery fabrication. More importantly, after the initial formation, the SEI film still acts as a barrier that prevents continuous electrolyte decomposition during the subsequent charge/discharge processes, which completely suppresses the gassing of graphite LIBs. One significant difference between LTO and graphite is the high lithium intercalation potential of LTO (1.5 V vs. Li+/Li), which is far higher than that of the SEI formation potential (0.6-0.8 V vs. Li+/Li). Therefore, an appropriate formation protocol is essential for providing a stable SEI on the LTO/C anode (at low potentials vs. Li+/Li) in order to prevent the irreversible and excessive consumption of electrolyte and lithium ions.

As shown in Fig. 4, in the initial charge stage of the full cell, the potential of LTO is maintained at about 1.5 V, and the inorganic components (mainly including Li2CO3 and LiF) of the SEI layer might be produced, as demonstrated in Fig. 3A. At the end of the charge stage of the full cell (i.e., the high potential formation region in Fig. 4), the potential of LTO can drop down to the SEI formation potential (~0.6 V). At this stage, the carbon-containing species in the SEI are mainly a mixture of Li2CO3 and PEO oligomers (-CH2-CH2-O)n, as shown in Figs. 3B and 3C. Their formation could be due to the decomposition of solvents, leading to the formation of a uniform coating layer (Fig. 4).

More importantly, it is generally accepted that an ideal SEI film should have the following properties: (1) high electrical resistance, high cation selectivity, and permeability; (2) a proper thickness with an intact structure; and (3) flexible properties, and tolerance to expansion and contraction stresses (since the SEI layer must accommodate the expansion and contracting sub-surfaces during cycling). Edström et al.32 described and demonstrated that the SEI has a heterogenic structure, which is composed of inorganic LiF and Li2CO3 close to the electrode surface and an organic polymeric component.
Figure 3. XPS spectra of LTO/C electrodes after different formation protocols: (A) 2.8 V formation, (B) 3.0 V formation and (C) 3.2 V formation. (a), (d), and (g) are C 1s spectra, (b), (e), and (h) are O 1s spectra, and (c), (f), and (i) are F 1s spectra.

Figure 4. Potential variation of cathode, anode, and LMO//LTO/C full batteries, and surface evolution of LTO/C electrode during formation.

Conclusions

For the purpose of suppressing the gas generation of LMO//LTO/C LIB systems, we have developed a high-potential formation protocol, which can result in a stable SEI film on the surfaces of LTO/C materials. It was found that, with the formation potential increased to above 3.0−3.2 V, a larger proportion of flexible PEO component was formed in the interface layer, which contributed to less gassing and improved cycling performance. Therefore, the high-potential formation protocol is very effective for suppressing the gas generation in the LTO battery, and this easy high-potential formation protocol makes LTO/C anode a very promising anode material for large-scale LIBs.

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