

Source Of Thermal Reactivity At The Positive And Negative Electrode In Lithium Batteries

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Introduction

Lithium ion rechargeable batteries possess high energy density and excellent power compared to other commercialized battery systems, which gives them a significant market as power sources for portable electronics such as cellular phones, laptop computers, etc. However, their application to electric vehicles (EV) and hybrid vehicles (HEV) have been limited because these applications need better thermal stability to reduce the safety risks. Safety issues generally occur if the cell exceeds the critical temperature above which the increase of the cell's temperature is irreversible (thermal runaway) due to the heat produced by the anode, cathode, electrolyte and their interactions above the critical temperature. In this paper we discuss the possible source of the thermal reactivity at both the positive and negative electrodes.

Positive Electrode

The study on the positive electrode was carried out using $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. In this case, the material was charged using both powder form (no binder or carbon additive) and as an electrode that includes binder and carbon additive. Figure 1 shows the DSC of fully charged powder using $\text{LiPF}_6/\text{EC}:\text{DEC}$ electrolyte. The onset temperature of the main peak takes place at 200°C , with 1050 J/g of heat generated during this reaction. This result is similar to that of the fully charged powder in the presence of solvents alone, such as EC and DEC. In addition, DSC of the fully charged electrode in the presence $\text{LiPF}_6/\text{EC}:\text{DEC}$ shows the same onset temperature (200°C) with the same amount of heat (1040 J/g) as in case of the charged powder with either electrolyte or solvent alone. When examining the decomposition of the charged electrode or the powder by thermal gravimetric analysis (TGA), we found that the material decomposes at 200°C and generates O_2 gas, which was detected by GC-MS. By taking into consideration all the above results, the main reaction that occurs at the positive electrode is oxidation of the solvent, involving oxygen generated by the delithiated oxide. An oxide that generates less oxygen or no oxygen would enhance the inherent safety of lithium ion batteries.

Negative Electrode

Figure 2 presents the DSC curves obtained from the lithiated carbon anode samples (obtained at 20% SOC intervals) at a scan rate of $10^\circ\text{C}.\text{min}^{-1}$ from 50°C to 400°C . It can be seen from this figure that only one exothermic peak is detected in the fully de-intercalated sample (Li_0C_6). This peak is broadened to a wide peak with more intercalated lithium (Li_xC_6 , $x \geq 0.18$). A peak starting at 269°C and reaching the maximum at 283°C is detected in the DSC scan of $\text{Li}_{0.37}\text{C}_6$. A DSC trace of $\text{Li}_{0.57}\text{C}_6$ is very similar to that of $\text{Li}_{0.37}\text{C}_6$. However, a new sharp peak at about 336°C is detected in the DSC curve for $\text{Li}_{0.71}\text{C}_6$. This sharp peak shifts to 301°C with more intercalated lithium ($\text{Li}_{0.91}\text{C}_6$).

The Li_0C_6 sample (0% SOC) contains graphite, SEI film, and the remaining electrolyte (mainly LiPF_6 and EC). The SEI film incorporates stable compounds (LiF , Li_2CO_3 and other inorganic compounds) and meta-stable components (e.g. lithium-alkyl carbonates). The meta-stable components are not stable at high temperatures, especially in the presence of Li atoms. The electrolyte employed here does not decompose and produce heat until 250°C . In addition, fresh graphite does not react strongly with electrolyte below 190°C . Therefore, this peak can only be attributed to the SEI breakdown.

The peak associated with the SEI film decomposition becomes broad with increasing intercalated lithium, as shown in

the curves for Li_xC_6 ($x \geq 0.18$). One possible explanation is that upon heating, the initial SEI is broken down exposing lithiated carbon to react with the electrolyte to form a new SEI. This process continues until the concentration of lithium in the carbon becomes small, which then produces a more stable lithiated carbon that doesn't react any further with the electrolyte to form SEI, because the lithium doesn't deintercalate. The exotherm that starts at 265°C could be due to electrolyte decomposition. A similar peak was observed when conducting a DSC of the electrolyte alone. The peak observed at 336°C is associated with the exfoliation of the exposed non-passivated carbon caused by the electrolyte. X-ray diffraction performed on the material, after DSC, clearly confirmed that the layered structure of carbon had totally collapsed and an amorphous phase was formed.

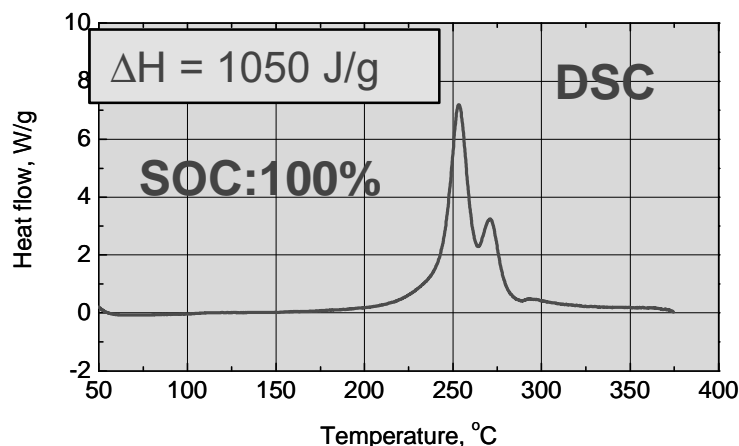


Figure 1. DSC of fully charged powder of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ without binder and carbon additive. The electrolyte used is $\text{LiPF}_6/\text{EC}:\text{DEC}$

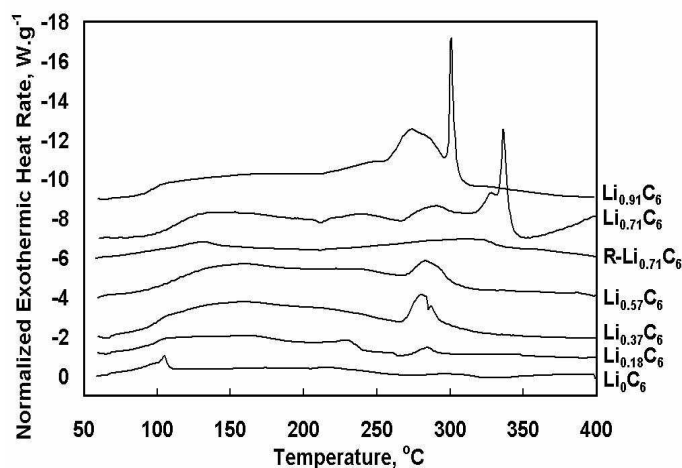


Figure 2. DSC curves of Mag-10 samples with different amounts of intercalated lithium at a scan rate of $10^\circ\text{C}.\text{min}^{-1}$. R- $\text{Li}_{0.71}\text{C}_6$ represents a graphite anode rinsed with DMC and vacuum dried to remove the remaining salt and EC

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