

Effect of Aluminum Doping on Impedance of Lithium-Ion Cells during Calendar Life Storage

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High-power lithium-ion batteries are under development for the Partnership for a New Generation of Vehicles (PNGV) program. We have found that cells made of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes and graphite anodes meet the PNGV power requirements at the early stage of cell cycling [1]. However, a substantial impedance rise occurs during accelerated aging and cycling at 40°C to 70°C , which leads to a power decline of the cells. Measurements using symmetrical-cell and reference-electrode approaches indicate that the increase of interfacial resistance on the cathode side dominated the total cell impedance rise during accelerated aging [2,3]. This increased interfacial resistance is likely associated with the formation of a surface layer, which results from either cathode decomposition at the surface or oxidation of the electrolyte at the cathode-electrolyte interface. Therefore, improving the cathode stability is the key to solving this problem. In this study, we will show that doping $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes with aluminum results in much better stability of the positive electrode, and suppression of the cell impedance rise during accelerated aging at 50°C and 80% state-of-charge (SOC) has been significantly suppressed.

In addition to non-doped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, three concentrations of Al-doping were investigated: $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ ($x = 0.01, 0.02, 0.05$). The positive electrode was made by mixing 84 wt% of active positive material with 8 wt% carbon additive and 8 wt% polyvinylidene fluoride (PVDF) binder dissolved in N-methylpyrrolidone. The negative electrode was made by mixing graphite (91 wt%) with PVDF binder (9 wt%). The electrolyte used for the electrochemical and aging test was 1M LiPF_6 in ethylene carbonate: diethyl carbonate (1:1). The aging test was carried out by charging each cell to 80% SOC and then storing it in an oven at 50°C . The area specific impedance (ASI) of the cell was monitored every week to track any changes that occur during the accelerated calendar-life testing.

Figure 1 shows the change in the ASI of these four cells during accelerated aging at 50°C . The ASI was measured by the current interruption method at about 80% SOC. When the cathode is made of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ without Al doping, the area specific impedance increased sharply during the first 10 days of storage and then stabilized. Same behavior is observed with a very small concentration of Al-doped $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ ($x = 0.01$). This phenomenon is due to the build-up of a resistive film at the surface of the cathode material, which increases the interfacial resistance of the positive electrode [2]. Once the film is formed, it acts as a barrier to prevent further reaction between the electrolyte and the cathode material at the electrode interface. As a result, no further film formation takes place, which leads to the observed stabilization of the ASI of the cell after 10 days aging. However, with Al-doped $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ ($x = 0.02, 0.05$), the fully charged composition becomes more

stable, especially with higher aluminum concentrations. Figure 1 shows that by increasing the Al doping level from 1% to 5%, the ASI of the cells stabilizes during the accelerated aging test. The cell made of the cathode with 5 wt% Al doping shows little increase in the area specific impedance after storage at 80% SOC and 50°C for more than 35 days. The stabilization of the $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ cathode is probably due to the strong Al-O bond, which makes the $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ rock-salt layered structure more resistive to a possible surface reaction with the electrolyte at the interface of the electrode.

In summary, a small amount of Al doping leads to a significant suppression of the impedance rise of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ /graphite cells during calendar life storage without sacrificing the cell capacity. This material could also be a good cathode material for high-power applications with longer calendar life.

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References

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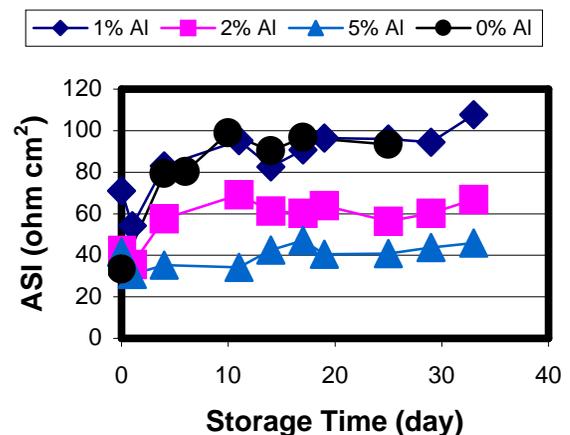


Figure 1. Changes in the ASI of $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ /graphite cells at 80% SOC with storage time at 50°C .