

LiNi_{0.5}Co_{0.5}O₂ as a long-lived positive active material for lithium-ion batteries

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Abstract

LiNi_{0.5}Co_{0.5}O₂ layered material could be a possible cathode material for advanced lithium-ion batteries in applications such as medical devices. The material was prepared by the co-precipitation method, which leads to a highly stoichiometric and homogeneous powder with a desirable particle size. It has shown reasonable cycling stability at a *C*/2 rate up to 100 cycles, and is expected to be much more stable at lower rates and capable of providing the needed capacity. We also showed that the use of lithium fluoroalkyl-phosphate Li[PF₃(C₂F₅)₃] salt-based electrolyte significantly improves the calendar life of the battery. Aging tests have been performed under severe conditions (storage at 50 °C and 4.1 V) clearly show a huge capacity loss for the conventional cathode LiNi_{0.8}Co_{0.2}O₂ while LiNi_{0.5}Co_{0.5}O₂ electrode exhibits a limited capacity fading. Finally, because it has less nickel content, differential scanning calorimetry (DSC) measurements confirm that LiNi_{0.5}Co_{0.5}O₂ is much safer than the LiNi_{0.8}Co_{0.2}O₂ cathode.

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1. Introduction

The LiNi_{1-x}Co_xO₂ ($0 \leq x \leq 1$) system has been extensively studied during the last decade in direct relation to the significant expansion of the lithium-ion battery market [1–7]. Within this system, LiNi_{0.8}Co_{0.2}O₂ has been given much attention as a possible positive electrode for consumer batteries [8,9]. This material, however, is more reactive and its lifespan could be limited to fewer than 3 years at ambient temperature. Therefore, it is not suitable for applications that require longer calendar life at higher temperatures, such as implantable medical devices, where the battery constantly operates at human body temperature. In this context, LiNi_{0.5}Co_{0.5}O₂ is suggested as an alternative cathode for this specific application, where cost is not a major barrier. In addition, LiNi_{0.5}Co_{0.5}O₂ is expected to be structurally and thermally much more stable than any other nickel-rich compound, especially after several cycles. LiNi_{0.5}Co_{0.5}O₂ is also expected to provide 150 mAh/g capacity at a cut-off voltage of 4.3 V. In this paper, we report the possibility of using LiNi_{0.5}Co_{0.5}O₂ as a positive active material combined with a lithium fluoroalkyl-phosphate Li[PF₃(C₂F₅)₃]-based

electrolyte for long-lived batteries that power medical devices.

2. Experimental

LiNi_{0.5}Co_{0.5}O₂ was synthesized by the co-precipitation method in an aqueous solution. This preparation method produces a very homogenous mixture of the precursors, and permits a suitable high ionic statistical distribution during thermal treatment [10]. First, 1 M aqueous solution of nickel and cobalt nitrates was prepared according to a Ni/Co = 1 molar ratio. The solution was then added to an ammoniacal solution of lithium hydroxide (1 M LiOH and 3 M NH₄OH) with a Li/(Ni + Co) = 1.05 molar ratio. A blue-green precipitate formed immediately. As mentioned, 5% excess lithium was added to prevent the well-known lithium loss phenomenon during high-temperature sintering. The solvents were eliminated at 70 °C by using a Rotavapor primary vacuum; the precipitate was then dried at 120 °C over 12 h. The resulting powder was heated progressively (2 °C/min) from room temperature up to 450 °C to allow complete decomposition of the starting materials. After grinding, the material was sintered at 750 °C for 24 h under an O₂ gas flow. The layered structure of the material was determined

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by X-ray diffraction (XRD) and its composition was confirmed by atomic absorption analysis.

A positive electrode was made by coating a paste of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ active material, acetylene black (Chevron55) and polyvinylidene fluoride (PVdF) binder (84:8:8 wt.%) on an aluminum-foil collector. Two kinds of electrolytes were used: 1 M LiPF_6 in a (1:1) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) solvents, labeled LP40, and 1 M $\text{Li}[\text{PF}_3(\text{C}_2\text{F}_5)_3]$ in (1:1) (EC:DEC), labeled LiFAP. Both electrolytes were provided by Merck Ltd. The negative electrode was prepared by mixing MCMB graphite with 17 wt.% SFG6 graphite and 8 wt.% PVdF binder; the resulting paste was spread on copper foil. The cells were assembled inside a helium-filled dry box and were evaluated using coin-type cells (CR2032: 1.6 cm^2). The charge/discharge measurements were carried out between 2.8 and 4.3 V potential range under 0.2 mA/cm^2 current density.

Accelerated aging tests were carried out on cells made of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ positive electrode, with graphite as a negative electrode and electrolytes. The cells were charged up to 4.1 V (almost 80% state of charge) and kept in an oven at 50°C . The capacity fade of the cells was monitored during storage. Similar accelerated aging tests were carried out on a conventional $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode using similar cell chemistry for the purpose of comparing its stability to that of the $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ cathode. Differential scanning calorimetry (DSC) was also performed on both $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ charged at 4.3 V to investigate their reactivity with the electrolytes and their impact on cell safety.

3. Results and discussion

The X-ray pattern of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ was indexed by assuming that the material has an $\alpha\text{-NaFeO}_2$ ordered structure (S.G. $R\bar{3}m$). The hexagonal lattice parameters, $a = 2.836 \text{ \AA}$ and $c = 14.079 \text{ \AA}$, were calculated by a Rietveld profile matching refinement option. In the context of this space group, lithium and 3d metal ions are in specific 3b (0, 0, 1/2) and 3a (0, 0, 0) sites, respectively; whereas oxygen atoms occupy 6c (0, 0, Z_{ox}) as a general position ($Z_{\text{ox}} \approx 0.25$). The resulting powders exhibit rock-shaped morphologies with particle sizes averaging $10 \mu\text{m}$ (Fig. 1).

Charge/discharge curves were recorded for the voltage window 2.8–4.3 V at C/50, C/8 and C/2 rates up to 100 cycles. Fig. 2 shows cycling data of cells made of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ cathode with a LiFAP electrolyte at room temperature. The first discharge capacity varies slightly, depending on the rate, but generally still averages 150 mAh/g . The irreversible capacity loss is about 25 mAh/g after the first discharge. At a rate of C/50, we notice an excellent reversibility of the cathode up to 75 cycles. At accelerated rates (C/8 and C/2), 85% of capacity retention is observed for both rates after 100 cycles, indicating good electrochemical behavior of the cathode despite the kinetic effect. A similar capacity loss

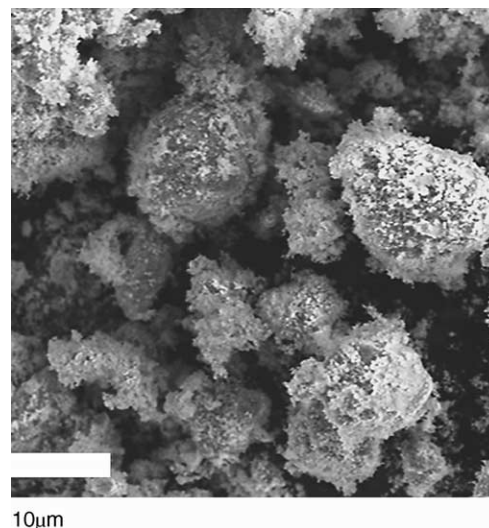


Fig. 1. SEM photograph of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$.

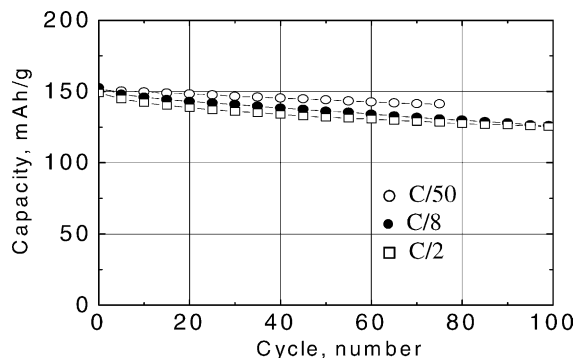


Fig. 2. Cycling data of full cells made of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ cathode with LiFAP electrolyte at different rates at room temperature.

profile is observed for cells filled with the LP40 electrolyte; the capacity retention, however, is slightly lower than that for the LiFAP electrolyte. This result could be due to the effect of the electrolyte, since all cells were strictly made under the same conditions. Indeed, LiFAP salt recently has been reported to provide electrolytes having good thermal and chemical stability with no HF acid generation in comparison

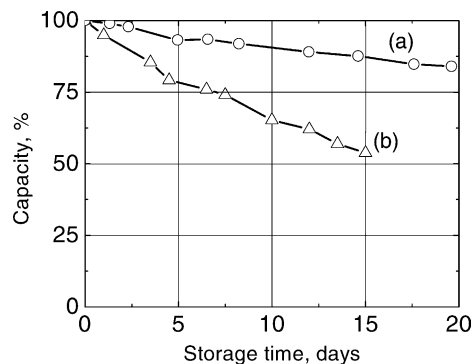


Fig. 3. Accelerated aging of cells made of (a) $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ and (b) $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (storage at 80% SOC; $T = 50^\circ\text{C}$).

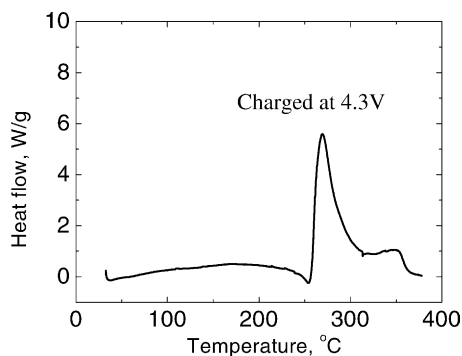


Fig. 4. DSC measurement of fully charged $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ cathode.

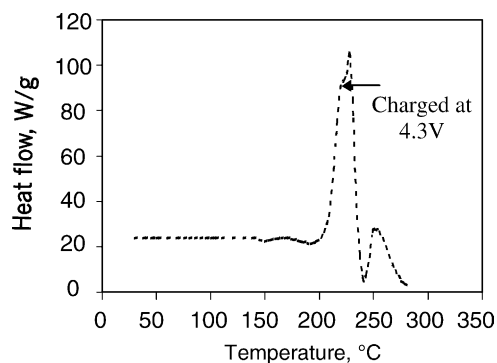


Fig. 5. DSC measurement of fully charged $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode.

with LiPF_6 salt. Therefore, a $\text{Li}[\text{PF}_3(\text{C}_2\text{F}_5)_3]$ -based electrolyte is expected to extend the life of the battery significantly [11].

Fig. 3 shows the result of an accelerated aging test of cells made of a carbon negative electrode and either a $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ or a $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ positive electrode (Fig. 3a and b). The capacity loss of the cell made of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ positive electrode reaches 50% after only 15 days of storage at 50 °C. However, the cell made of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ shows a much lower fading rate, with only 16% capacity fade after 20 days of storage at 50 °C. This result clearly indicates that $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ has better stability than $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The fast capacity fade for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ could be due to the large concentration of highly oxidizing tetravalent Ni^{4+} generated at 80% state of charge, which could easily reduce to a more stable and inactive NiO phase, leading to an irreversible loss of capacity due to a loss of the active material. Actually, the capacity fade phenomenon has to be seen as a failure of the whole battery system beyond the evident failure of the cathode itself. Indeed, at 50 °C the unstable hypothetical Ni^{4+}O_2 phase becomes more reactive with the electrolyte, which possibly leads to the oxidation of the latter and limits its performance during the subsequent cycles. In addition, from a crystallographic point of view, it is well known that nickel-rich cathodes are less stable because of some structural rearrangements that can occur at a high state of charge, which leads to an irreversible behavior of cell chemistry [1].

Thermal stability of the $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ electrode charged at 4.3 V was tested by performing differential scanning calorimetry measurements, as shown in Fig. 4. In the presence of the LP40 electrolyte, only a very negligible exothermic peak at around 270 °C is observed. However, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ charged at the same state of charge presents a significant exothermic reaction with the electrolyte at a much lower temperature of 210 °C (Fig. 5). This result clearly confirms that the amount of oxygen generated from the decomposition of the electrodes is much higher in the case of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrode, which leads to its high reactivity with the electrolyte; the $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ electrode, however, shows good thermal stability and therefore could provide better safety performance.

4. Conclusion

$\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ positive active material can be prepared easily by the co-precipitation method, which leads to spherical-shaped particles. Combined with lithium a fluoroalkyl-phosphate $\text{Li}[\text{PF}_3(\text{C}_2\text{F}_5)_3]$ salt-based electrolyte and graphite anode, the $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ positive electrode has shown an acceptable electrochemical behavior, i.e. good cyclability and an enhanced calendar life. This result attests to the role that the electrolyte can play in lithium-ion battery cell chemistry. We showed that $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ ages better than the conventional cathode $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, which is a sign of its high stability, confirmed by DSC measurements. Therefore, the choice of the cell chemistry presented here could be suggested for lithium-ion batteries designated for use to power medical devices.

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