



Failure mechanism of layered lithium-rich oxide/graphite cell and its solution by using electrolyte additive



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HIGHLIGHTS

- Cyclability of layered lithium-rich oxide/graphite cell depends on cathode performance.
- HF formed from electrolyte decomposition causes the corrosion of aluminum current collector.
- TMSPi is effective for improving cyclability of layered lithium-rich oxide/graphite cell.
- Cathode interphase formed from TMSPi suppresses the electrolyte decomposition.

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ABSTRACT

We report a failure mechanism of layered lithium-rich oxide/graphite cell and a solution to this failure. Charge/discharge tests demonstrate that $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ /graphite full cell fails when it is performed with cycling and this issue can be solved effectively by using an electrolyte additive, tris (trimethylsilyl) phosphite (TMSPi). Further cycling tests on $\text{Li}/\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ and $\text{Li}/\text{graphite}$ half-cells and physical characterizations on the cycled cathode indicate that this failure involves the increased HF concentration and the subsequent corrosion for aluminum current collector of cathode due to the electrolyte decomposition during cycling. TMSPi contributes to the formation of a protective interphase on cathode due to its preferential oxidation compared with the base electrolyte, which suppresses the electrolyte decomposition and the HF formation, preventing aluminum current collector from corrosion.

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1. Introduction

In the past decades, lithium-ion battery has been dominating power source market in electronic devices such as portable telephones, laptop computers and cameras [1–3]. Owing to its advantages including higher energy density and longer cycle life than other secondary batteries, lithium ion battery arouses intensive interest for its applications in electric vehicles [4,5]. In this new application area, the energy density of currently commercialized lithium ion battery needs to be enhanced [6,7]. Therefore, much

attention has been paid to the cathode and anode materials with larger specific capacity, especially the cathode materials with high working potential [8,9]. Layered lithium-rich oxide is an interesting cathode material for high energy density lithium ion battery because it could deliver far larger specific capacity (over 250 mAh g^{-1}) under high potential than conventional cathode materials including LiCoO_2 and LiFePO_4 [10,11]. However, the application of layered lithium-rich oxide is limited by the poor cyclability in practice. Generally, the failure of layered lithium-rich oxide is attributed to the structural destruction of the oxide during cycling [12], and at the high working potential, the conventional carbonate-based electrolytes for lithium ion battery use are unstable thermodynamically and tend to decompose oxidatively [1,13].

To solve these problems, much effort has been made in the past

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decade. Partial substitution of the transition metal in layered lithium-rich oxide with Mg, Mo, Al, Ti, Cr, Fe, or Ru, has been performed to stabilize the surface and bulk phase structure of the layered lithium-rich oxides [14–23]. He et al. reported that the capacity retention of a layered lithium-rich oxide, $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, was improved by doping Zr from 40% to 74% after 100 cycles (at 1C between 2.5 and 4.6 V) [21]. Obviously, doping does not yield a significant cyclability improvement and cannot suppress electrolyte decomposition. Coating with inert oxides (Al_2O_3 , MgO , MnO_x , TiO_2) [23–29], fluorides (AlF_3) [30,31], and phosphates (AlPO_4 , CoPO_4) [32,33] provides a protection for layered lithium-rich oxides and suppresses electrolyte decomposition to some extent [34]. However, coating is not cost-effective because the procedure is complicated and introducing inert compounds reduces the specific capacity of layered lithium-rich oxides. Additionally, more stable solvents, such as dinitriles [35–37], sulfones [38–40], ionic liquids [41–43] and lactone [44], have been considered for replacing carbonate solvents, whereas these applications cause new issues such as the deteriorated interfacial compatibility between electrolyte and electrode materials and the decreased ionic conductivity of electrolyte [41].

Recently, much attention has been paid to a new approach, forming a protective interphase on cathode oxides by using electrolyte additives, which is similar to but more cost-effective than coating [45–51]. The preferential oxidation of the additives compared to the electrolyte is necessary because earlier oxidation of the additives ensures that the protective cathode interphase is formed without the incorporation of the electrolyte decomposition products and subsequently suppresses the electrolyte decomposition. The electrolyte decomposition takes place in the form of the complexes between solvent carbonate molecules and salt anion PF_6^- , generating HF [52,53]. The resultant HF might attack the cathode oxides and even cause the corrosion of aluminum current collector, which is detrimental to the cyclability of the cathode, but less attention has paid to this issue. Therefore, the preferential oxidation of the additives is important to mitigate the damage of lithium ion battery from electrolyte decomposition [54]. Phosphites and phosphates are often used as electrolyte additives to form protective cathode interphase for high voltage cathodes [46,47,51]. Comparatively, phosphites are oxidized more easily because they contain unsaturated bonds. Moreover, silicon-containing compounds are believed to be effective as electrolyte additives for high voltage cathode due to the contribution of silicon to the chemical stability of cathode interphase [48]. With the advantages of phosphite and silicon, it can be expected that silicon-containing phosphites can be effective for the cyclability improvement of layered lithium-rich oxides.

In this study, we report a failure mechanism of layered lithium-rich oxide/graphite battery and the solution to this failure by applying electrolyte additive. A representative layered lithium-rich oxide, $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, and a silicon-containing phosphite, tris (trimethylsilyl) phosphite (TMSPi), were considered. The detailed failure mechanism and the contribution of TMSPi to the cyclability of the battery were understood by electrochemical measurements and physical characterizations.

2. Experimental section

2.1. Electrode preparation and cell assembly

$\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ electrode was prepared by coating the slurry of 80 wt% $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ (Shenzhen BTR New Energy Resources Material Co., Ltd), 10 wt% acetylene carbon black (TIMCAL Ltd, Switzerland), 10 wt% poly (vinylidene fluoride) (PVDF, Oflourine Chemical Tech Co., Ltd, China) binder on Al foil and dried

in vacuum oven. Graphite electrode was prepared by the mixture of 89 wt% artificial graphite (Dongguan Kaijin New Energy Technology Co., Ltd, China), 4 wt% Ks6 (Timrex), 2 wt% Super-p (MMM carbon, Belgium) and 5 wt% polyvinylidene difluoride (PVDF, Oflourine Chemical Tech Co., Ltd, China) binder in *N*-methyl-2-pyrrolidone. The mixture was coated, pressed on to a copper foil current collector and dried in vacuum oven. Tris (trimethylsilyl) phosphite (TMSPi) was purchased from Alfa Aesar Technology Co. Battery-grade carbonate solvents and lithium hexafluorophosphate (LiPF_6) were provided by Guangzhou Tinci Materials Technology Co., Ltd, China. All these chemicals were used without further purification. 1.0 M LiPF_6 in ethyl methyl carbonate (EMC)/ethylene carbonate (EC)/diethyl carbonate (DEC), EMC/EC/DEC = 5:3:2, in weight, was used as the base electrolyte. TMSPi (0.5 wt%) was added into the base electrolyte to prepare TMSPi-containing one. Microporous membrane (Celgard 2400) was used as the separator. $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ /graphite CR2025-coin cell was assembled with a capacity ratio of 1/1.3 for cathode/anode based on 200 mAh g^{-1} for $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ and 350 mAh g^{-1} for graphite. Li/ $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ and Li/graphite half-cells were assembled in CR2025 type coin cell with lithium foil as anode. To confirm the formation of HF from the electrolyte decomposition, a transparent V-type Li/ $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cell was also assembled. All the electrolyte preparations and the cell assemblies were conducted in an Ar-filled glove box (MBraun, Germany) where the water and oxygen contents were controlled less than 0.1 ppm.

2.2. Electrochemical measurements and physical characterizations

Charge/discharge tests were performed on LAND system (CT2001A, Wuhan, China). The content of HF in the electrolyte was determined by titration. 0.01 M NaOH in deionized water and 0.001 wt% bromothymol blue as indicator were used. The cycled cells were disassembled in the Ar-filled glove box. Both the lithium foil and $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ electrodes were taken out, rinsed with anhydrous DMC for three times to remove the residual EC, EMC, DEC and LiPF_6 , and then dried overnight under vacuum at room temperature for physical characterizations. X-ray diffraction was carried out on BRUKER D8 ADVANCE (Germany) with monochromatized Cu $K\alpha$ radiation. Transmission electron microscopy was performed on JEM-2100HR (Japan) and scanning electron microscopy was on JSM-6510 (Japan). The contents of Ni, Co, Mn and Al deposited on Li foils were analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima 8300, USA). Fourier transition infrared spectrum was taken from Bruker Tensor 27 (Germany) within 600–2000 cm^{-1} . Surface compositions on the cycled cathode were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, USA), using a focused monochromatized Al $K\alpha$ radiation ($h\nu = 1486.6$ eV) under ultra high vacuum with the spot size of 400 μm and energy step size of 1.000 eV. The final adjustment of the energy scale was made based on the graphite peak at 284.8 eV. The XPS analyses were performed without sputtering.

3. Results and discussion

3.1. Cyclic performance of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ /graphite full cells

Fig. 1A presents cyclic performances of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ /graphite full cells in the base and TMSPi-containing electrolytes at 0.2 C for the first cycle and at 0.5 C for the subsequent cycles between 2.0 and 4.8 V. It can be seen from Fig. 1A that the cell in the base electrolyte experiences fast capacity decay: from 197 mAh g^{-1} initially to 134 mAh g^{-1} at the 50th cycle with a capacity retention

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