

Short communication

# Expanding performance limit of lithium-ion batteries simply by mixing $\text{Al}(\text{OH})_3$ powder with $\text{LiCoO}_2$

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## Abstract

Mixing a small amount of  $\text{Al}(\text{OH})_3$  powder with a  $\text{LiCoO}_2$  cathode material is demonstrated to improve markedly the cycle performance and thermal stability of commercial grade  $\text{LiCoO}_2$ /graphite lithium-ion batteries.  $\text{Al}(\text{OH})_3$ -mixed  $\text{LiCoO}_2$ /graphite prismatic cells exhibit excellent capacity retention as high as 95% after 400 cycles with negligible polarization build-up. Moreover, the thermal stability of the cells is greatly improved by  $\text{Al}(\text{OH})_3$  mixing, which is confirmed by higher residual and recovery capacity ratios after storage at 90 °C compared with a pristine cell. The beneficial effects of  $\text{Al}(\text{OH})_3$  are found to be related mainly to an improvement of the cathode side, which is ascribed to reduced unwanted side-reactions with the electrolyte.

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## 1. Introduction

Electric vehicles (EVs) and hybrid electric vehicles (HEVs) require their energy storage devices to exhibit cycle-lives comparable with the vehicles themselves [1], which presents a great challenge for lithium-ion batteries (LIBs). Because the degradation of LIBs is related mainly to the irreversible reactions at the electrode/electrolyte interfaces [2], vast efforts have been devoted to the surface modification of electrode materials in order to extend the performance limits of LIBs. In particular, surface coating of conventional cathode materials with inert metal oxides ( $\text{MO}_x$ ,  $M = \text{Al}$  [3],  $\text{Mg}$  [4],  $\text{Sn}$  [5],  $\text{Zn}$  [6],  $\text{Zr}$  [7]) and inorganic salts ( $\text{AlF}_3$  [8],  $\text{Al}(\text{OH})_3$  [9],  $\text{AlPO}_4$  [10]) has been reported to improve markedly the structural stability and cycleability of the cathode materials, although the nature of the coating effects is still controversial [11,12]. The surface coating, however, makes the preparation process complex, adds production costs, and causes homogeneity issues in large-scale synthesis.

Recently, it has been claimed that simple mixing of  $\text{Li}_3\text{PO}_4$  powder with a  $\text{LiCoO}_2$  cathode greatly improves the high-voltage performance of all-solid-state lithium–polymer batteries [13]. The result is intriguing because it suggests the possibility that simple mixing methods can replace rather complex coating processes. Most of the above reports on cathode modification are based, however, on the results obtained by using coin-type cathode/Li half-cells, which are quite different from practical cathode/carbon full cells. Contrary to cathode/Li half-cells, cathode/carbon full cells are more vulnerable to the deterioration caused by irreversible side-reactions because the amount of available Li is limited [14]. This study discloses the dramatic effects of  $\text{Al}(\text{OH})_3$  as a novel inorganic cathode additive on the cycle performance and the thermal stability of commercial grade  $\text{LiCoO}_2$ /graphite cells.

## 2. Experimental

For battery-performance tests, 863448-size (nominal capacity of 1100 mAh) and 633450 (nominal capacity of 1000 mAh) prismatic cells were employed. Battery grade 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (1/2, v/v) was used as the electrolyte solution. Mesocarbon microbeads graphite (25  $\mu\text{m}$  average diameter, Osaka Gas, Japan) was

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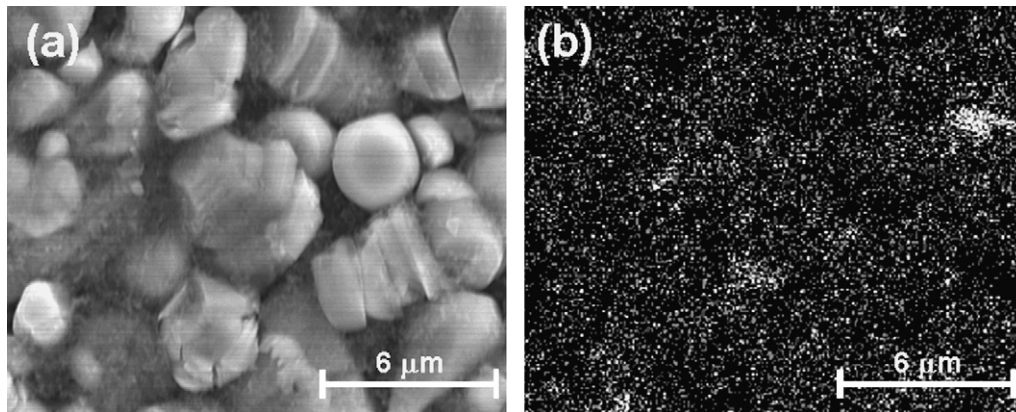


Fig. 1. (a) SEM micrograph and (b) Al mapping image of 5 wt.%  $\text{Al}(\text{OH})_3$ -mixed  $\text{LiCoO}_2$  cathode sheet.

used as the anode material. The cathode was prepared by mixing  $\text{LiCoO}_2$  (90 wt.%, 5  $\mu\text{m}$  diameter, NCI/Japan) and  $\text{Al}(\text{OH})_3$  powder (5 wt.%, 0.8  $\mu\text{m}$  diameter, Martinswerk) in a *N*-methyl pyrrolidinone solution containing 2.5 wt.% polymer binder and 2.5 wt.% conductive carbon. Relatively even distribution of  $\text{Al}(\text{OH})_3$  powder among  $\text{LiCoO}_2$  particles was confirmed through an Al mapping technique with scanning electron microscopy (Fig. 1). The cells were cycled at 23 °C over a 3–4.2 V range with a 0.5 C constant charging current followed by 4.2 V constant voltage charging and a 0.5 C constant discharging current. Prior to an oven storage test, the cells were cycled several times and fully charged on the last cycle. The oven temperature was raised from room temperature to 90 °C in 1 h, kept at 90 °C for 4 h, and then decreased back to room temperature in 1 h. Electrochemical impedance spectroscopy (EIS) was performed with a frequency response analyzer (Solartron 1260) combined with a potentiostat (EG&G Princeton Applied Research 273A). The frequency range was 10 kHz to 0.1 Hz and the amplitude of the a.c. signal was 5 mV.

### 3. Results and discussion

Fig. 2 compares the capacity retention during 400 cycles of a 863448-size prismatic cell (1100 mAh) of  $\text{Al}(\text{OH})_3$ -mixed  $\text{LiCoO}_2$ /graphite (hereafter called  $\text{Al}(\text{OH})_3$  cell) and a pristine  $\text{LiCoO}_2$ /graphite cell (hereafter simply called pristine cell). Due to the inactive nature of  $\text{Al}(\text{OH})_3$ , the  $\text{Al}(\text{OH})_3$  cell gives a slightly decreased capacity on the first cycle compared with the pristine cell. Similarly, an initial loss in specific energy is inevitable for cells employing surface-coated cathode materials when the amount of coating material is usually in the range of 1–5 wt.%. The slight initial capacity loss in the  $\text{Al}(\text{OH})_3$  cell, however, is overcompensated by markedly improved cycleability. Note that the  $\text{Al}(\text{OH})_3$  cell exhibits only 5% capacity loss after 400 cycles, while the pristine cell loses 14% of its initial capacity. Considering that the cycleability of the pristine cell itself is one of the finest records among present state-of-the-art LIBs, the cycle performance of the  $\text{Al}(\text{OH})_3$  cell is a significant breakthrough towards extremely reliable LIBs

to the best of our knowledge. Moreover, the  $\text{Al}(\text{OH})_3$  cell shows a negligible change in the discharge profile with prolonged cycling, whereas the pristine cell suffers from a relatively higher build-up of polarization (Fig. 3). This indicates that the  $\text{Al}(\text{OH})_3$  cell also exhibits excellent power retention, which

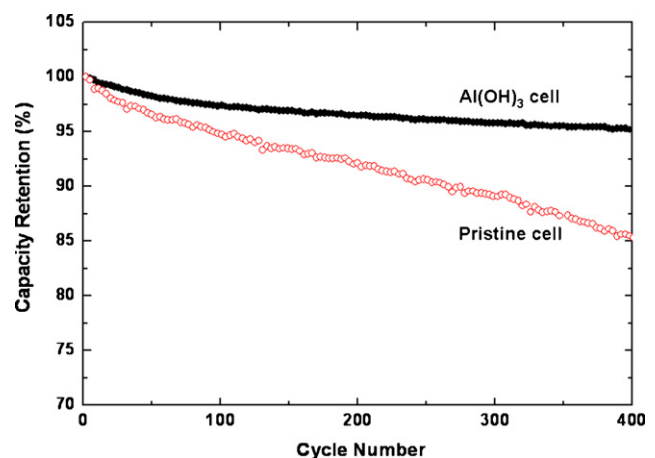


Fig. 2. Comparison of cycleability of 863448-size prismatic cells (nominal capacity of 1100 mAh) consisting of pristine  $\text{LiCoO}_2$ /graphite or  $\text{Al}(\text{OH})_3$ -mixed  $\text{LiCoO}_2$ /graphite.

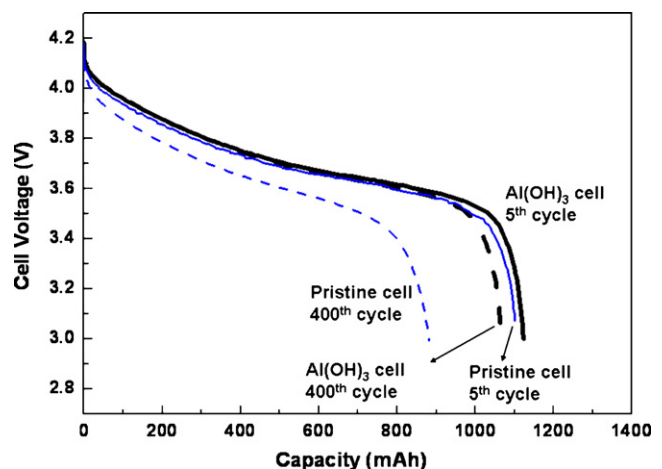


Fig. 3. Discharge profiles at 5th and 400th cycles of cells tested in Fig. 2.

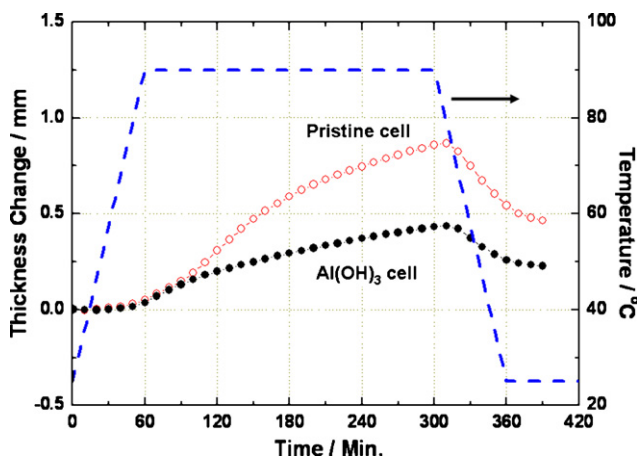


Fig. 4. Thickness changes during oven storage of 633450-size prismatic cells (1000 mAh) of (a) pristine LiCoO<sub>2</sub>/graphite and (b) Al(OH)<sub>3</sub>-mixed LiCoO<sub>2</sub>/graphite.

is one of the critical requirements for application in EVs and HEVs.

Not only the cycleability, but also the thermal stability of the LIBs is greatly improved by Al(OH)<sub>3</sub> mixing. Fig. 4 compares the swelling behaviour of fully charged 633450-size prismatic cells (1000 mAh) during 90 °C oven storage. Note that the increase in thickness of the Al(OH)<sub>3</sub> cell is approximately half of that of the pristine cell. In addition, the Al(OH)<sub>3</sub> cell exhibits a higher residual and recovery capacity ratio after the oven storage (86.9 and 88.6%, respectively) than the pristine cell (80.2 and 81.6%, respectively). Data obtained from electrochemical impedance spectroscopy (EIS) before and after oven storage are presented in Fig. 5. Note that there is no conceivable change in

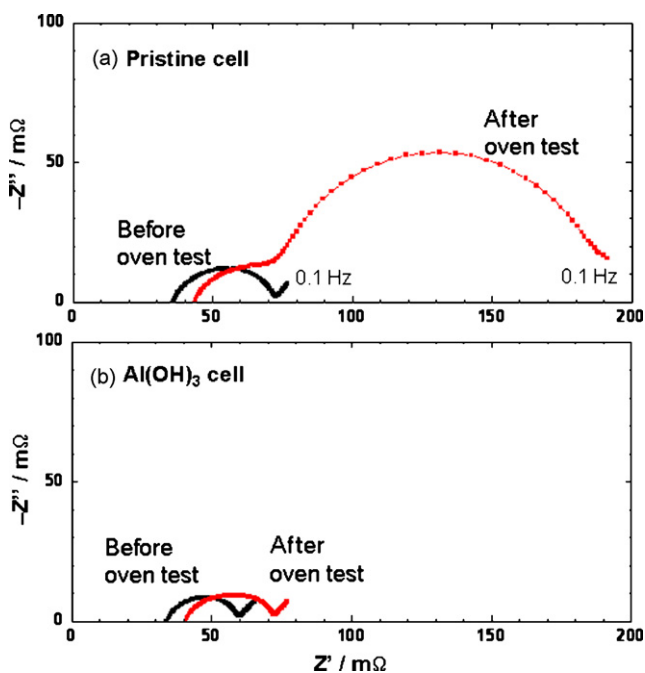


Fig. 5. EIS plots of 633450-size prismatic cells (1000 mAh) of (a) pristine LiCoO<sub>2</sub>/graphite and (b) Al(OH)<sub>3</sub>-mixed LiCoO<sub>2</sub>/graphite before and after storage at 90 °C.

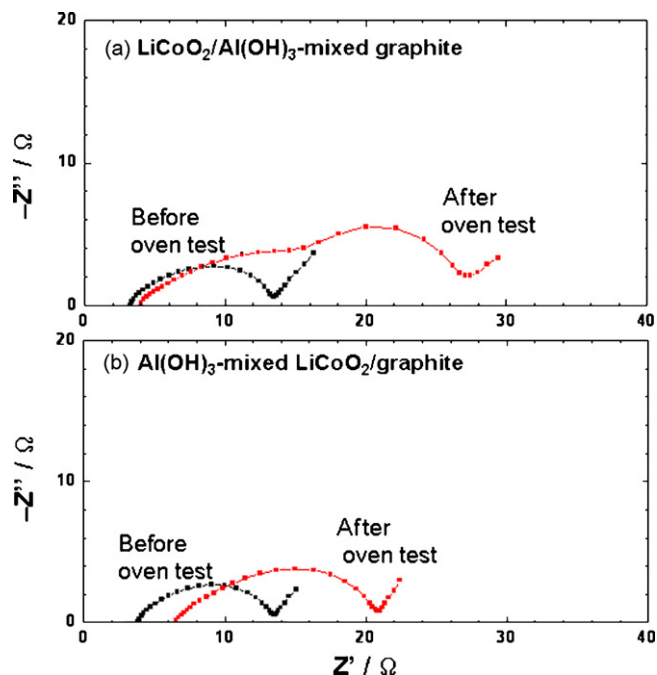


Fig. 6. EIS plots of 2032 coin-type cells (4 mAh) of (a) LiCoO<sub>2</sub>/Al(OH)<sub>3</sub>-mixed graphite and (b) Al(OH)<sub>3</sub>-mixed LiCoO<sub>2</sub>/graphite before and after storage at 90 °C.

the total impedance of the Al(OH)<sub>3</sub> cell after oven storage except for a slight increase in the x-axis intercept that represents the electronic and ionic resistances (Fig. 5b). By contrast, a significant rise in impedance is observed for the pristine cell (Fig. 5a), which is due mainly to the increased semi-circle at lower frequencies related to the faradaic charge-transfer. It appears that the improved thermal stability of the Al(OH)<sub>3</sub> cell should be ascribed to reduced degradation in the cathode|electrolyte interface because Al(OH)<sub>3</sub> is added to the cathode only.

In order to elucidate further the effects of Al(OH)<sub>3</sub> on the cathode and anode, two types of 2032 coin-type cell were prepared, namely, 2.5 wt.% Al(OH)<sub>3</sub>-mixed LiCoO<sub>2</sub>/graphite and LiCoO<sub>2</sub>/5 wt.% Al(OH)<sub>3</sub>-mixed graphite. Fig. 6 exhibits the EIS results of the cells before and after the 90 °C oven storage. The impedance rise in the Al(OH)<sub>3</sub>-mixed LiCoO<sub>2</sub>/graphite cell after the oven storage is much less than that in the LiCoO<sub>2</sub>/Al(OH)<sub>3</sub>-mixed graphite cell. Therefore, it seems that the beneficial effects of Al(OH)<sub>3</sub> are related mainly to improvement of the cathode side.

With regard to the origin of the Al(OH)<sub>3</sub> effect on cathode performance, it appears useful to refer to case of Al<sub>2</sub>O<sub>3</sub> coating. Cho et al. [3] proposed that the coating layer suppresses lattice expansion of Li<sub>x</sub>CoO<sub>2</sub> during cycling. Dahn et al. opposed Cho's explanation and attributed the improved performance to the reduction in the contact area between LiCoO<sub>2</sub> and electrolyte [11] and the fresh LiCoO<sub>2</sub> surface after heat-treatment [12]. More recently, it has also been suggested that the physico-chemical interaction between the coating material and the electrolyte plays an important role, which scavenges HF in the electrolyte to reduce metal dissolution from cathode materials [15,16], or forms solid superacids to enhance ionic conduction at the cathode surface [17]. Because physical sepa-

ration by compact coating layers or thermal refreshment should be excluded in our case, we conclude that the improvements gained by  $\text{Al}(\text{OH})_3$  mixing are related to the interaction with the electrolyte, although it is difficult to determine their exact nature at present.

It seems highly probable that the  $\text{Al}(\text{OH})_3$  effect depends on the characteristics of the  $\text{Al}(\text{OH})_3$  powder employed (such as particle size or crystalline structure) that are undergoing systematic surveys in our group. It is also expected that the initial capacity loss due to the dead volume of  $\text{Al}(\text{OH})_3$  powder in the cathode electrode can be minimized through optimizing its dose. More importantly, we are currently extending the mixing method to other metal oxides or compounds that have been found to be beneficial coating materials.

#### 4. Conclusions

It is demonstrated that the cycle performance and thermal stability of commercial grade  $\text{LiCoO}_2$ /graphite lithium-ion batteries can be greatly improved simply by mixing a small amount of  $\text{Al}(\text{OH})_3$  powder with a  $\text{LiCoO}_2$  cathode material. The gain is no less than that given by costly and complex surface coating processes, which should be a significant breakthrough towards highly reliable and economic lithium-ion batteries. We also consider that the mixing method can be extended to various inorganic powder/conventional cathode couples other than  $\text{Al}(\text{OH})_3$ / $\text{LiCoO}_2$ .

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