Stability of Li$_2$CO$_3$ in cathode of lithium ion battery and its influence on electrochemical performance

Yujing Bi,$^{a,b,d}$ Tao Wang,$^c$ Meng Liu,$^a$ Rui Du,$^{a,b}$ Wenchao Yang,$^a$ Zixuan Liu,$^a$ Zhe Peng,$^a$ Yang Liu,$^a$ Deyu Wang$^{a,*}$ and Xueliang Sun$^d$

Lithium carbonate is an unavoidable impurity at the cathode side. It can react with LiPF$_6$-based electrolyte and LiPF$_6$ powder to produce LiF and CO$_2$, although it presents excellent electrochemical inertia. Samples of Li$_2$CO$_3$-coated and LiF-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ were prepared to compare their influence on a cathode's behavior. After 200 cycles at 1C, in contrast to 37.1% of capacity retention for the Li$_2$CO$_3$-coated material, the LiF-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ retained 91.9% of its initial capacity, which is similar to the fresh sample. This demonstrates that decomposition of Li$_2$CO$_3$ can seriously deteriorate cyclic stability if this occurs during working.

### Introduction

Lithium ion batteries (LIB) are the most successful electrochemical energy storage technology of recent decades. As a chemical system, the performance of LIB is influenced by impurities, including species introduced by the components or in situ generated during working.$^{1-5}$ A good understanding of their chemical behavior and influence on cell performance is important in development of high-quality commercial batteries.

At the cathode side, impurities of lithium carbonate are unavoidable because of the carbonate-based electrolyte and the meta-stability of cathode materials.$^{6-9}$ Li$_2$CO$_3$ has good electrochemical inertia, thus it is considered as a suitable component for construction of the cathode's protective layer.$^{10-12}$ However, its appearance is often accompanied by serious capacity fading of cathode materials, especially for nickel rich layer oxides.$^{13-16}$ To the authors’ knowledge, this contradiction in the role of lithium carbonate has not been carefully investigated to date.

Here we research the stability of lithium carbonate on the cathode side, and its influence on electrochemical performance of LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$O$_2$. Although it possesses excellent electrochemical inertia, the exposed Li$_2$CO$_3$ particles react easily with LiPF$_6$-based electrolyte and LiPF$_6$ powder to generate LiF, CO$_2$, and POF$_3$. For a comparison, samples of Li$_2$CO$_3$-coated and LiF-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ were prepared. In contrast to the poor cyclic stability of Li$_2$CO$_3$-coated material, LiF-coated samples present much better cyclic stability, which is similar to the fresh pristine material.

### Experimental section

LiPF$_6$ (Kanto Chemical Co., Inc., 99%), LiTFSI (MMM, Ltd, 98%), and Li$_2$CO$_3$ (Aladin, >99%) were dried at 120 °C under vacuum in a transfer chamber of an Ar-glove box for 48 h before use. An electrolyte of 1 mol L$^{-1}$ LiPF$_6$ dissolved in mixed solution of propyl carbonate (PC) and dimethyl carbonate (DMC) (1 : 1, v/v) (Guotai Huarong Chemical New Material Co., Ltd) was used as received.

The chemical stability of Li$_2$CO$_3$ was evaluated by immersing the powder material (1 g) in 5 mL electrolyte, sealing in Al-plastic packages, and then heating at 30 °C, 55 °C, 80 °C, and 100 °C for 12 h in an Ar-glove box. Powders of Li$_2$CO$_3$ (0.49 g) and LiPF$_6$ (2 g) were also mixed and sealed in Al-plastic packages to heat at 80 °C for 12 h. To check the interactions between water and LiPF$_6$, 10 mL H$_2$O was slowly dropped onto 2 g LiPF$_6$ powder. Moreover, 2 g LiPF$_6$ powder was fast dissolved into 10 mL H$_2$O.

LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ was synthesized by the high-temperature solid-state method as published.$^{16,17}$ The Li$_2$CO$_3$-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ was obtained by storing LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ at 55 °C with saturated stream (15 kPa) in a desiccator for 1 month. The LiF-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ was prepared by immersing the Li$_2$CO$_3$-coated sample in electrolyte and heating at 80 °C for 12 h.

The electrode was composed of cathode material, super P and polyvinylidenefluoride (PVdF) at weight ratio 8 : 1 : 1 suspended in NMP, and the slurry was casted on aluminum foil current collectors. The electrode was dried at 120 °C under
a vacuum for 12 h and then punched into φ 16 mm disks. CR2032 coin cells were assembled with the prepared electrode as cathode, lithium foil as anode, Celgard 2550® as separator, and 1 mol L\(^{-1}\) LiPF\(_6\) in a mixture solution of polycarbonate (PC)/dimethyl carbonate (DMC) (1 : 1, v/v) as the electrolyte. Cell assembly was performed in an Ar-filled M-Braun glove box, in which H\(_2\)O and O\(_2\) were controlled less than 1 ppm. Linear sweep voltammetry between 2.5 and 5.5 V vs. Li/Li\(^+\) at 0.1 mV s\(^{-1}\) rate was carried out at an electrochemical work station (Solartron, 1470E). Electrochemical measurements were performed on a battery tester of Land 2001A (Wuhan, China) between 2.8 and 4.3 V vs. Li/Li\(^+\) at 25 °C at various rates.

The powders were characterized by X-ray diffraction with a Bruker D8 advanced diffractometer using CuK\(\alpha\) (\(\lambda = 1.5406\) Å) radiation (Bruker AXS, D8 Advance) between 10° and 60° by 0.02° steps. Analysis of microscopy was performed by scanning electron microscopy (SEM, Hitachi, S4800) and transmission electron microscopy (TEM, FEI, Tecnai F20, 200 kV). Surface analysis was conducted with a PHI 3056 X-ray photoelectron spectrometer (XPS), which was excited by Mg K\(\alpha\) radiation at a constant power of 100 W (15 kV and 6.67 mA). The gas species were analyzed on a gas chromatograph mass spectrometer (GC-MS, Agilent 7890B-5977A, EI). The column of GC is a capillary column chromatograph (Agilent, HP-PLOT/U).

**Results and discussion**

The purchased lithium carbonate could be attributed to the C2/c space group of monoclinic system with particle size at 2–10 μm, as shown in Fig. 1a. This has good electrochemical inertness, with decomposition reaction peaking at \(~5.3\) V vs. Li/Li\(^+\) as shown in Fig. 1b. Clearly, Li\(_2\)CO\(_3\) is electrochemically stable inside the lithium ion cells at current working conditions.

The chemical stability of Li\(_2\)CO\(_3\) was evaluated via experiment with a mixture of 1 g Li\(_2\)CO\(_3\) and 5 mL electrolyte sealed in an Al-plastic package and heated at 30 °C, 55 °C, 80 °C, and 100 °C. When treated at 30 °C, the signal of Li\(_2\)CO\(_3\) is gradually weakened over time, as shown in Fig. 2a. In contrast, LiF peaks are detectable after 2 days of storage, and their intensities are strengthened after 30 days. As the temperature increases to 55 °C, lithium fluoride is one of the dominant phases after 12 h heat treatment. In the sample treated at 80 °C and 100 °C after 12 h, LiF becomes the single crystalline phase (Fig. 2b). This indicates that Li\(_2\)CO\(_3\) should react chemically with LiPF\(_6\) to generate lithium fluoride as the solid product.

The generated gas in the package is tested by GC-MS. In all tested packages, CO\(_2\) and POF\(_3\) are the extremely dominant gaseous species, with a ratio more than 90%, as demonstrated.
in Fig. 2c. Carbon dioxide could be decomposed from Li$_2$CO$_3$, and POF$_3$ could be attributed to reaction of the PF$_6^-$ group with a trace amount of moisture. Small chromatographic peaks at 9, 13, and 16.2 min would be caused by corrosion of HF. Combined with the XRD results, lithium carbonate should be reacted spontaneously with electrolyte to generate LiF as the solid product, and CO$_2$ and POF$_3$ as the gaseous species.

To further explore the probable reason for this reaction, a mixture of Li$_2$CO$_3$ and LiPF$_6$ (1 : 1 in mole) powder was sealed and heated at 80 °C for 12 h. The tested pack ages were inflated quickly. The solid remnant is LiF and the dominant gaseous products are POF$_3$ and CO$_2$, indicating the reaction between solids is the same as for Li$_2$CO$_3$ with electrolyte. This result indicates that the Li$_2$CO$_3$ decomposition could be preceded by direct attack of LiPF$_6$ without the assistance of moisture, as shown in Pathway 1, because both salts were thoroughly dried before the test.

Pathway 1: LiPF$_6$ + Li$_2$CO$_3$ → POF$_3$ + CO$_2$ + 3LiF

According to the LiPF$_6$ production procedure, it should contain trace amount of HF, which could react with lithium carbonate to produce water. Although PF$_6^-$ groups can react with water in organic media, they are also quite stable in aqueous solution, e.g., NaPF$_6$ aqueous solution is used as the source of PF$_6^-$ in synthesis of ionic liquids. The stability of LiPF$_6$ powder with a small amount of water, the situation in this case, has not been discussed to the authors’ knowledge.

Here dissolution behavior of LiPF$_6$ salt (2 g) in water (10 mL) was compared with experiments of quickly pouring LiPF$_6$ powder into water and slowly dropping water into LiPF$_6$ powder. In the first case, a clear solution was formed with a pH value of ~5, as shown in Fig. 2d1. In the second case, smoke was released when water encountered LiPF$_6$ powder. After dropping, the solution still contains some insoluble material, as demonstrated in Fig. 2d2, which is lithium fluoride, as identified by XRD. The pH value of the solution is ~2, indicating that H$^+$ was generated during dissolving. This demonstrates that LiPF$_6$ tends to decompose with a small amount of H$_2$O to generate H$^+$. The probable reason for this phenomenon is that PF$_6^-$ ion group could not form a stable hydration layer with the small amount of H$_2$O. Therefore, a trace amount of HF may catalyze decomposition of lithium carbonate with H$^+$ as the catalyst, as shown in Pathway 2. This mechanism is possible, although we tend to believe Pathway 1 is more likely.

Pathway 2: 2H$^+$ + Li$_2$CO$_3$ → 2Li$^+$ + CO$_2$ + H$_2$O

LiPF$_6$ + 2Li$^+$ + H$_2$O → POF$_3$ + 2H$^+$ + 3LiF

The chemical stability of Li$_2$CO$_3$ with LiTFSI electrolyte and LiTFSI powder was also evaluated to compare the influence of cations. No obvious inflation was observed after storing at 80 °C for 12 h, indicating that Li$_2$CO$_3$ decomposition could be related to the PF$_6^-$ group. As no candidate exhibits the possibility of totally replacing LiPF$_6$ in commercial systems, chemical decomposition of lithium carbonate appears unavoidable when directly exposed to electrolyte. A good understanding of its influence on cathode's performance would be helpful in construction of high-quality cells. As Li$_2$CO$_3$ is relatively easy to generate on the surface of nickel-rich content cathodes, LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ was selected as the target to prepare Li$_2$CO$_3$-coated and LiF-coated samples in the following comparison.

To accelerate the Li$_2$CO$_3$ generation rate, a LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ sample was placed in a glass dish and stored in a desiccator with water at 55 °C for 1 month. The glass jar was opened daily to ensure the CO$_2$ content. As shown in Fig. 3a and b, the signal of Li$_2$CO$_3$ was detected with XRD and XPS afer humidity corrosion. And TEM identified the decomposing layer with a thickness of ~18 nm in Fig. 3g. This demonstrates that the sample after humidity corrosion is Li$_2$CO$_3$-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$.

According to the previous results, the Li$_2$CO$_3$-coated sample was mixed with electrolyte and heated at 80 °C for 12 h to prepare a LiF-coated sample. As shown in Fig. 3a, Li$_2$CO$_3$ totally

![Fig. 3](image_url)
disappeared, and LiF became the only detectable impurity after this treatment. The weak broadened peak from 687.5 to 689.0 eV in Fig. 3c may be attributed to Li\textsubscript{x}PO\textsubscript{y}F\textsubscript{z}\textsuperscript{25} during the heat process in the electrolyte.\textsuperscript{25} From the TEM images (Fig. 3g and i), it can be seen that the dense Li\textsubscript{2}CO\textsubscript{3} layer changes to the porous LiF membrane. These results indicate that LiF-coated LiNi\textsubscript{0.8}Co\textsubscript{0.1}Mn\textsubscript{0.1}O\textsubscript{2} was obtained after the electrolyte attack, which is consistent with the previous results (Scheme 1).

The electrochemical performances of the as-synthesized, Li\textsubscript{2}CO\textsubscript{3}-coated and LiF-coated LiNi\textsubscript{0.8}Co\textsubscript{0.1}Mn\textsubscript{0.1}O\textsubscript{2} were compared, as shown in Fig. 4. The discharge capacity of the fresh sample was 192.5 mA h g\textsuperscript{-1}. The discharge capacity of Li\textsubscript{2}CO\textsubscript{3}-coated sample dropped to 170.5 mA h g\textsuperscript{-1} (Fig. 4a). As the discharge plateau is almost overlapped at the initial part, the lost capacity should correspond to the loss of active material rather than polarization. With this hypothesis, the decomposition ratio should be \( \sim 12\% \). After the electrolyte attack, sample capacity recuperated to 174.2 mA h g\textsuperscript{-1}. This is probably related to the relatively low molecular weight of lithium fluoride. The rate performance shows the same trend, as shown in Fig. 4b. The fresh, Li\textsubscript{2}CO\textsubscript{3}-coated, and LiF-coated samples deliver 150.3, 124.1, and 132.0 mA h g\textsuperscript{-1} at 5C, respectively.

All samples were cycled under 1C rate, their results are compared in Fig. 4c. The fresh material maintains 149.1 mA h g\textsuperscript{-1}, 87.2% of the initial capacity after 200 cycling. The discharge capacity of the Li\textsubscript{2}CO\textsubscript{3}-coated sample seriously fades, only 37.1% is retained after the 200th cycle. In contrast, the LiF-coated sample still presents 143.5 mA h g\textsuperscript{-1}, namely 91.9% of the initial discharge capacity, in the 200th cycle.

This improvement on cyclic stability for LiF-coated LiNi\textsubscript{0.8}Co\textsubscript{0.1}Mn\textsubscript{0.1}O\textsubscript{2} is related to the reaction of Li\textsubscript{2}CO\textsubscript{3} decomposition. According to the results in the former part, if reacted inside the cell, the gaseous species of Li\textsubscript{2}CO\textsubscript{3} decomposition should be adsorbed on the surface of the cathode material. Gas adsorption decreases the active surface area and gradually aggregates the cell’s polarization. A similar phenomenon is observed on a zinc electrode, where the over-potential is quickly augmented by H\textsubscript{2} absorption.\textsuperscript{26,27} As for the LiF-coated sample, the interface between cathode and electrolyte is not affected by the generated gas, therefore it presents cyclic stability.

### Conclusion

The role of Li\textsubscript{2}CO\textsubscript{3} in LiPF\textsubscript{6} electrolyte was investigated in this study. Although it is electrochemically stable, Li\textsubscript{2}CO\textsubscript{3} can be chemically decomposed to LiF as a solid product, CO\textsubscript{2} and POF\textsubscript{3} as gaseous species. The generated gaseous species can be absorbed on the cathode surface, causing aggregation of discharge polarization and deteriorating cyclic stability. As Li\textsubscript{2}CO\textsubscript{3} impurity cannot be well controlled in practical production, treatment at high temperature to release the gas should be very helpful to maintain the cell’s cyclic stability.

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### References