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Stable, fast and high-energy-density $LiCoO_2$ cathode at high operation voltage enabled by glassy B_2O_3 modification

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HIGHLIGHTS

- $LiCoO_2$ powders are modified with glassy B_2O_3 through H_3BO_3 decomposition.
- High-voltage (4.5 V) cycling stability and rate capability are greatly improved.
- Lithium boron oxide (LBO) as major SEI part is formed on the surface after cycling.
- B_2O_3-modification mitigates high-voltage induced interfacial side reactions.
- The as-formed 3D glassy LBO enhances the kinetics of the electrode.

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ABSTRACT

In this work, commercial $LiCoO_2$ is modified with a glassy B_2O_3 by solution mixing with H_3BO_3 followed by post-calcination in order to enhance its high-voltage electrochemical performance. The glassy B_2O_3 coating/additive is believed to serve as an effective physiochemical buffer and protection between $LiCoO_2$ and liquid electrolyte, which can suppress the high-voltage induced electrolyte decomposition and active material dissolution. During the early cycling and due to the electrochemical force, the as-coated B_2O_3 glasses which have 3D open frameworks tend to accommodate some mobile Li^+ and form a more chemically-resistant and ion-conductive lithium boron oxide (LBO) interphase as a major component of the solid electrolyte interphase (SEI), which consequently enables much easier Li^+ diffusion/transfer at the solid-liquid interfaces upon further cycling. Due to the synergetic effects of B_2O_3 coating/modification, the high-voltage capacity and energy density of the B_2O_3-modified $LiCoO_2$ cathode are promisingly improved by 35% and 30% after 100 cycles at 1 C within 3.0–4.5 V vs. Li/Li^+. Meanwhile, the high-rate performance of the B_2O_3-modified electrode is even more greatly improved, showing a capacity of 105 mAh g^{-1} at 10 C while the bare electrode has dropped to no more than 30 mAh g^{-1} under this rate condition.

1. Introduction

The increasing demand for high-energy-density lithium-ion batteries (LIBs) has motivated huge efforts to explore high-performance electrode materials. Since commercialization of LIBs, $LiCoO_2$ has being dominating the cathode market due to its easy production and good cycling stability [1–4]. Though various new classes of materials have been developed in the last decades, $LiCoO_2$ still has vast superiority as small-format power units for portable devices considering its highest tapping density and maturity in

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battery production among all candidates. As the base material of other layered cathodes and a classical model material for mechanism studies, $LiCoO_2$ has being receiving unfailing research interest in both experimental and theoretical aspects [5–11].

In recent years, the focus of research in $LiCoO_2$ has shifted to the application at high voltages [9], which can increase the degree of Li^+ utilization in the lattice structure and thus push up the limit of its capacity and energy density. Previously, $LiCoO_2$ batteries were charged to a cut-off potential no more than 4.2 V vs. Li/Li^+, delivering only half of its theoretical capacity (274 mAh g^{-1}) and energy density (~1000 Wh Kg^{-1}, estimated with a constant voltage of 3.9 V vs. Li anode). When the potential is elevated to 4.5 V, the initial discharge capacity and energy density of $LiCoO_2$ can be increased to 190 mAh g^{-1} and 700 Wh Kg^{-1} at 1 C (~70% utilization), which is very promising for next-generation applications. Unfortunately, pure $LiCoO_2$ is not stable and its rate capability also becomes very poor under such high-voltage conditions. Multiple reasons are believed to accounted for the high-voltage degradation of $LiCoO_2$, such as oxidization decomposition of the liquid electrolytes, structure collapse, Co^{4+} dissolution and oxygen release from the active materials, and fast accumulation of the so-called solid electrolyte interphase (SEI) which is electrochemically irreversible and kinetically unfavorable [12–14].

To address the high-voltage issues of $LiCoO_2$, numerous attempts have been devoted which can be classified into three strategies: 1) using additives in electrolytes [15,16], 2) lattice element doping [11,17] and 3) surface coating/modification with another active/inactive materials [9,18–20]. In the aspect of surface coating, particular attention has been paid to the use of some large band-gap oxides such as Al_2O_3 [21–23], ZrO_2 [24], TiO_2 [22,25] and ZnO [26–28]. Take the most attractive Al_2O_3 coating that has been universally applied for many other electrode materials for example, the improvements of the cycling stability and rate performance of $LiCoO_2$ are mainly ascribed to the formation of a $LiAlO_2$-$LiCoO_2$ solid solution on the particle surface which can release elastic stains, provide Li^+ pathways and avoid oxygen loss from $LiCoO_2$ [29–32]. In addition to the use of metal oxides, some solid electrolyte materials (e.g. Li_2CO_3 [33] Li_3PO_3 [34], LiPON [35] and $Li_4Ti_5O_{12}$ [36]) in polycrystalline or amorphous forms have also been used to modify $LiCoO_2$ taking advantages of their high electrochemical stability and ion-conducting property, the latter is supposed to be important to enhance the interfacial kinetics of $LiCoO_2$ electrode.

Compared with the numerous studies on metal oxide coatings, there are few reports regarding the use of non-metallic oxides for surface coating/modification of $LiCoO_2$. B_2O_3 is an interesting candidate for study since it comes from the same group of Al_2O_3 and similarly has a large band-gap and high chemical stability in acid condition due to strong B-O bonding. B_2O_3 is normally known as a glassy material with 3D networks allowing the conduction of ions in it. This property makes it a very important solid electrolyte material, e.g. as a glass former in Li_2O-B_2O_3-P_2O_5 [37,38] or as a ion-conduction promoter in $LiTi_2(PO_4)_3$ [39] and $LiTiO_2$ [40]. In the aspect of surface modification, Su et al. [41] reported effectively restricted sulfur or iodine dissolution in B_2O_3-modified Li-S and Li-I_2 batteries. B_2O_3 addition was also reported to be able to greatly influence the electrochemical performance of some carbon-based anodes (hard carbon [42,43], graphite [44] and graphene [45]) due to the change the electronic structure of these materials by partial B doping. Furthermore, the giant volume change in Si [46] and SnO_2-based [47,48] anodes can be well accommodated by B_2O_3 modification thanks to the 3D glassy feature of B_2O_3. Considering the high band-gap, high chemical stability and the 3D ion-conduction properties, B_2O_3 is supposed to be a promising surface modification material for addressing the high-voltage problems of $LiCoO_2$. Previously, B_2O_3 was used to modify $LiCoO_2$ through the solid-state synthesis and the electrochemical performance was studied with the cut-off voltage of 4.2 V [49]. However, there has been no report in literature regarding the high-voltage (>4.2 V) electrochemical performances of $LiCoO_2$ with B_2O_3 modification.

In this work, B_2O_3-modified $LiCoO_2$ cathode materials are synthesized by a facial and scalable solution-mixing/post-calcination method using H_3BO_3 as the precursor modifier. The electrochemical performances of the B_2O_3-modified electrodes are investigated at the cut-off potential of 4.5 V vs. Li/Li^+. It is found that both the cycling stability and the rate capability of the electrode are significantly improved by the B_2O_3 modification. The high-voltage induced side reactions at the electrode-electrolyte interfaces are effectively mitigated due to effective physiochemical protection from the B_2O_3 coating/additive. The enhancement of the rate capability is attributed to the electrochemical formation of a special glassy lithium boron oxide (LBO) interface as the major component of the SEI, which enables easier transfer of Li^+ and reduces the interfacial resistance during the long-term high-voltage cycling.

2. Experimental

2.1. B_2O_3-modification of $LiCoO_2$

1.5 g $LiCoO_2$ powders (99.9%, Hunan Changyuan Like Co., Ltd.) were put into a prepared transparent H_3BO_3 solution followed by strong stirring at room temperature (RT) for 1 h. The mixture was then heated to and slowly evaporated at 90 °C until a viscous slurry was formed, which was then dried at 80 °C in air for 12 h. Finally, the obtained product was calcined at 500 °C for 12 h in air in order to decompose the H_3BO_3. For a comparative study, 1 wt. %, 2 wt. % and 3 wt. % H_3BO_3 (with respect to the weight of $LiCoO_2$) was employed and the resulted samples are named as LCO/BO1, LCO/BO2 and LCO/BO3, respectively. Additional $LiCoO_2$ powders were treated with all the same procedures only without the addition of H_3BO_3 and the obtained sample is named as LCO-bare as the reference.

2.2. Electrode preparation and cell assembly

The bare or B_2O_3-modified $LiCoO_2$ powders were thoroughly mixed with acetylene black (AB) conductive additive and polyvinylidene fluoride (PVDF) binder with a weight ratio of 8: 1: 1 in N-methyl pyrrolidone (NMP). The slurry was homogeneously spread onto a piece of clean Al foil followed by vacuum-drying at 110 °C for 12 h. The electrode foil was punched into discs of 10 mm in diameter with a loading density of ~1.5 mg cm^{-3}. For electrochemical tests, CR2032-type coin cells were assembled in an Ar-filled glove-box using Li foil as the anode. Prior to the cell assembly, the electrodes and separators (polypropylene, Celgard 2400) were dried at 110 °C and 50 °C overnight in vacuum, respectively. 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) (1:1:1, v/v) was used as the liquid electrolyte.

2.3. Electrochemical tests

Galvanostatic charge/discharge tests of the half cells were performed using a CT2001A cell test instrument (LAND Electronic Co.) within 3.0–4.5 V vs. Li/Li^+ at RT. All cells were activated by a cycle of low-rate (0.2 C, 1 C = 140 mA g^{-1}) charge/discharge before the stability test at 1 C. The rate capability was tested stepwise from 0.02 C to 10 C and back to 0.02 C again. Cyclic voltammetry (CV) tests were carried out using an Arbin BT2000 equipment with a